CHEMISTRY IN INDUSTRY

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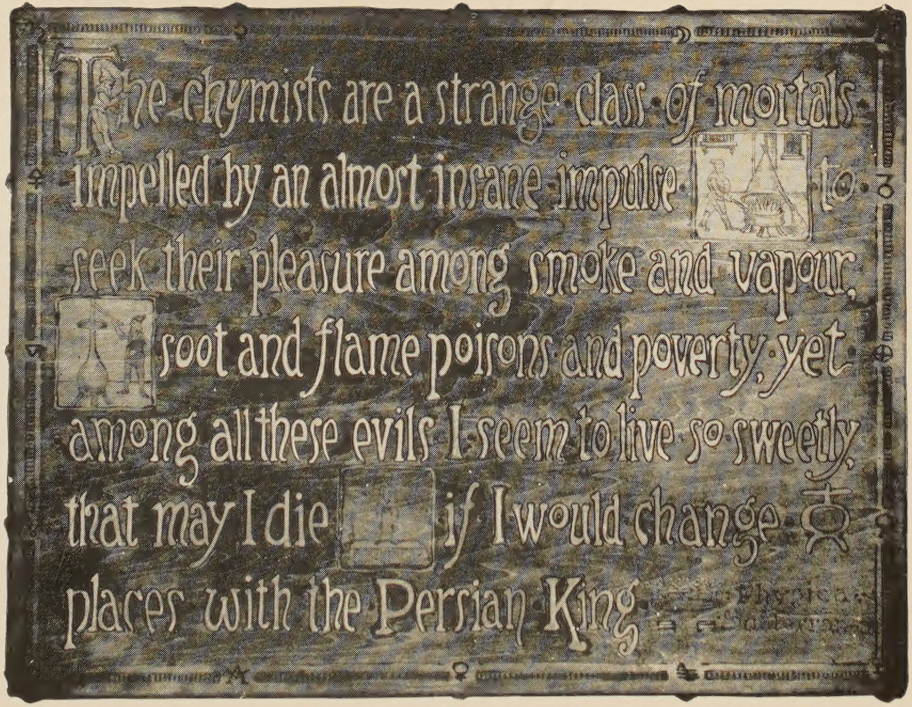
The chymists are a strange class of mortals
impelled by an almost insane impulse
to
seek their pleasure among smoke and vapour,
soot and flame poisons and poverty; yet
among all these evils I seem to live so sweetly
that may I die
if I would change
places with the Persian King

The above is a quotation taken from ''Acta Laboratorii Chymica Monacensis, seu Physica Subterranea'' (1669), by Johann Joachim Becher (phlogistonist).

CHEMISTRY IN INDUSTRY

A COÖPERATIVE WORK INTENDED TO GIVE EXAMPLES OF THE CONTRIBUTIONS MADE TO INDUSTRY BY CHEMISTRY

EDITED BY

H. E. HOWE

Chairman, American Chemical Society Committee on Prize Essays
Editor, Industrial and Engineering Chemistry

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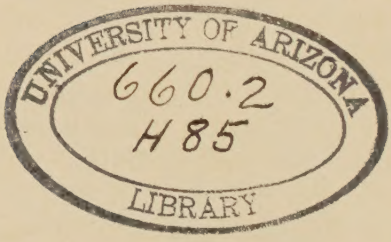

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FOREWORD

The ease with which any of the natural sciences can demonstrate how indispensable it is to modern life is simply a testimonial to the complexity of our civilization. However important the various sciences and the fields of engineering which deal with their applications may be, it is certain that chemistry shares with physics and mathematics the really fundamental positions.

Since chemistry deals with the changes of matter and its characteristics and properties under a wide variety of conditions, it is to be expected that its work can be traced in all forms of human endeavor. Indeed, someone has defined chemistry as the science which fashions from the materials found in Nature other substances which are better suited to the present needs of men. Another has stressed that work of the chemist which, aided by the electric current, enables him to do in a few moments many of the things which, to the best of our belief, Nature has required long ages to perform.

To stress the omnipresence of chemical work, a speaker at a meeting of business men offered to spend the time allotted in discussing the relation of chemistry to any object in the room that might be named, or its application to the business represented by any individual present. This feat is not so difficult to perform as might be imagined, for, lacking any other suggestions, the speaker could always discuss the chemical reactions upon which life itself is dependent, the chem-

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ical composition of the human body, the foods consumed, the clothing worn, and the tools with which the daily tasks are performed. Just imagine going through your day's work or pleasure robbed of those things which modern science has provided. We will not enumerate them here, but trust that after reading this book you will have no difficulty in appreciating how chemistry, unheralded, is everywhere about you.

I have often quoted a few paragraphs by H. N. Casson, Editor of *Efficiency Magazine,* which indicate one way in which the importance of chemistry to individuals may be stressed. The same story might be told in a variety of ways:

"What does chemistry mean to me?" said Mr. Narrowhead as he looked at this page, printed with ink made by a chemical process, on paper made by a chemical process.

As he pushed back his cuff, bleached by a chemical process, and laced his shoes made of leather, tanned by a chemical process, he glanced through a pane of glass, made by a chemical process, and saw a baker's cart full of bread, leavened by a chemical process, and a draper's wagon delivering a parcel of silk, made by a chemical process.

He pulled out his pencil, made by a chemical process, and wrote a reminder in his notebook bound by imitation morocco, made by a chemical process.

Then he put on his hat, dyed by a chemical process, and stepped out upon the pavement of asphalt, compounded by a chemical process, bought a daily paper with a penny refined by a chemical process, and proceeded to the office where he dealt in a certain chemical compound called coal.

"No," he added, "of course not, chemistry has nothing to do with me."

Notwithstanding the universal application of the data established by fundamental research, the Committee on Prize Essays of the American Chemical Society learned during the contest of 1923-1924 that the relation of chemistry to industry had not been set down in language easily understood, nor in places conveniently accessible to the thousands of students who

desired to write upon that topic. Consequently, it was decided to provide at least one reference book that would be of assistance, and this book is the result. It is in reality a symposium to which twenty-one specialists in as many different industries have contributed chapters dealing with what chemistry has accomplished in their field of work and noting several unsolved problems to indicate a few of the many opportunities that await the resourceful, well-grounded chemist.

It will be obvious that but a few of the industries that might be represented have been included in this volume. Had all the industries that deserve a place been accorded chapters we would have had, not a single volume, but a set of books in which would have been recorded the history of industrial development. It is hoped that the industries selected may be considered typical, and perhaps if this book achieves its purpose a companion volume may appear at a later date.

The editor takes this opportunity to express the deep appreciation of the Committee on Prize Essays of the American Chemical Society for the generosity which marked the coöperation of busy men who devoted time and effort to the preparation of these several chapters; also to members of his staff who assisted in editing, proof-reading, and performing the numerous other duties necessary in assembling a work of this character.

The Editor.

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CHEMISTRY IN INDUSTRY

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CHAPTER I

THE FOUNDATIONS OF CHEMICAL INDUSTRY

Robert E. Rose

Director, Technical Laboratory, E. I. du Pont de Nemours & Co.

Prelude: The Jugglers

All of us have seen the juggler who entertains by throwing one brightly colored ball after the other into the air, catching each in turn and throwing it up again until he has quite a number moving from hand to hand. The system which he keeps in motion has an orderly structure. He changes it by selecting balls of different colors, altering the course or the sequence of the balls, or by adding to or diminishing the number with which he plays.

With this figure in mind let us use our imaginations. Before us we have an assemblage of hundreds of thousands of jugglers varying in their degree of accomplishment; some handle only one ball, others, more proficient, keep several in motion, and there are still others of an astounding dexterity who play with an hundred or more at once. The balls they handle are of ninety different colors and sizes. The jugglers do not keep still but move about at varying rates; those handling few and light balls move more quickly than

those handling many or heavier ones. These dancers bump into each other and when they do so in certain cases they exchange some of the balls which they are handling or one juggler may take all of those handled by another, but in no case are the balls allowed to drop.

THE VANISHING POINT

Now imagine the moving group to become smaller and smaller until the jugglers cease to be visible to us, even when they dance under the highest power microscope. If someone who had not seen them were to come to you and say that he proposed undertaking the problem of finding out how the balls were moving and what were the rules of the exchanges made, and further that he proposed utilizing his knowledge to control what each minute juggler was doing, you would tell him that his task was hopeless. If the chemist had listened to such advice there would be no chemical industry and you would lose so much that you would not be living in the way you are.

The jugglers are the electromagnetic forces of matter, the balls are the atoms, and each group in the hands of the juggler is a molecule of a substance. In reality, of course, instead of each molecule being represented by one unit we should multiply our jugglers by trillions and trillions.

THE MASTERY OF MOLECULES

The chemist, without even seeing them, has learned to handle these least units of materials in such a way as to get the arrangements which are more useful from those less useful. This power he has acquired as the outcome of his life of research, his desire to understand, even though understanding brought him no material gain, but mere knowledge. Because of his

patience and devotion he has built a number of industries; all have this in common—they serve to rearrange atoms of molecules or to collect molecules of one kind for the service of man.

THE GREAT QUEST

The study of the substances of the earth's crust, of the air over and of the waters under the earth, which has led us to our present knowledge of the electron, atom, and molecule, has been more adventurous than many a great journey made when the world was young and the frontier of the unknown was not remote from the city walls. Into the unknown world of things upon the "sea that ends not till the world's end" the man of science ventured, and he came back laden with treasure greater than all the gold and precious stones ever taken from the earth. He gave these to others and he fared forth again without waving of flags, without the benediction of holy church, with no more than the courage of him who would win Nature, who had chosen a harder road than that of the great, made famous because of subduing other men. He took no arms upon his quest, scarcely enough food to keep body and soul together, but instead, fire, glass, and that most astounding of all tools, the balance. As he pushed farther and farther on his great venture and as more and more joined his little band, he brought more and more back to those who did not understand in the least what he was doing, until now the lives of all men are made easier if not happier by these strange, most useful, and most potent things of which he is the creator by reason of the understanding his journeys have given him—a power much greater than any mere black magic.

This is the story of some of the strange treasure found by him in the far lands that are about us—treasure found by learning the secret of the jugglers' dance—the dance of the least little things out of which all we know is fashioned.

Sulfuric Acid

THE GREAT DISCOVERY

In Sicily and other parts of the earth where there are volcanoes, lumps of a yellow crumbly "stone" are found, called brimstone (a corruption of *brennisteinn* or burning stone). This material was regarded as having curative properties; if it was burned in a house the bad odors of the sickroom of primitive times were suppressed. Also the alchemists found that it took away the metallic character of most metals and they considered it very important in their search for the philosopher's stone, the talisman that was to turn all things to gold. The alchemists found also that sulfur, when burned over water, caused the water to become acid, and one of them found further that if the burning took place in the presence of saltpeter the acid which was produced was much stronger; indeed, if concentrated it was highly corrosive. A useless find, it seemed, of interest only to the alchemist who hoped to become rich beyond the dreams of avarice, and immortal as the gods. But the chemist made this discovery of more importance to the condition of the human race than that of Columbus, because by it he gave man a kingdom different from any that could have been his by merely discovering what already existed upon earth. That is the wonder of the chemist's work; he finds that which is not upon the earth until

he discovers it; just as the artist creates so does the chemist. If he did not, there would be no chemical industry to write about.

EXPERIMENT TO MANUFACTURE

Having investigated this acid, he found it a most valuable new tool with which many new and interesting things could be made, and much could be done that before had been impossible. It became necessary, then, if all men were to profit as the chemist always wishes them to do by his power, that sulfuric acid should be made easily and cheaply in large quantities. The first attempt at commercial manufacture was in 1740; before that each experimenter made what little he needed for himself. The process, that mentioned above, was carried out in large glass balloons. It was a costly method and tedious. Then in 1746 lead chambers were substituted for the glass and the industry progressed rapidly.

The whole object of this most basic of all chemical industries can be written in three simple little equations.

Sulfur		Oxygen		Sulfur Dioxide
S	+	O_2	=	SO_2
Sulfur Dioxide		Oxygen		Sulfur Trioxide
SO_2	+	O_2	=	SO_3
Sulfur Trioxide		Water		Sulfuric Acid
SO_3	+	H_2O	=	H_2SO_4

Of the three elements necessary, oxygen occurs uncombined in the air of which it forms one-fifth by volume; it is also present combined with other elements in very large quantities in water, sand, and generally

throughout the earth's crust, which is nearly half oxygen in a combined condition.

THE RAW MATERIALS

The great storehouse of hydrogen on the earth is water, of which it forms one-ninth, by weight. Sulfur is not so widely distributed in large quantities but it is very prevalent, being present in all plants and animals and also in such compounds as Epsom salts, gypsum, and Glauber's salt. In the free condition, i.e., as sulfur itself, it is found in volcanic regions and also where bacteria have produced it by decomposing the products of plant decay. There is one other source of sulfur that is quite important, a compound with iron which contains so much sulfur that it will burn.

The problem then was to take these substances and from them group the elements in such order as to produce sulfuric acid.

Since sulfur burns readily, that is, unites with oxygen to form sulfur dioxide, one might expect it to take up one more atom of oxygen from the air and become sulfur trioxide. It does, but so slowly that the process would never suffice for commercial production. But there is a way of speeding up the reaction which depends on using another molecule as a go-between, thus making the oxygen more active. The principle is that of the relay. Suppose an out-fielder has to throw a ball a very long way. The chances are that the ball will not be very true and that it may fall short of reaching the base. If there is a fielder between, he can catch the ball and get it to the base with much greater energy.

The chemist uses as a go-between or catalyst (in one process), oxides of nitrogen. Molecules of this gas throw an oxygen atom directly and unfailingly into

any sulfur dioxide molecule they meet, then equally certainly they seize the next oxygen atom that bumps into them and are ready for the next sulfur dioxide molecule. Since molecules in a gas mixture bump into each other roughly five billion times a second, there is a very good chance for the exchange to take place in the great lead chambers of approximately a capacity of 150,000 cubic feet into which are poured water molecules (steam), oxygen molecules (air), and sulfur dioxide, to which are added small quantities of the essential oxides of nitrogen.

THE ACID RAIN

A corrosive, sour drizzle falls to the floor and this is chamber acid. It is sold in a concentration of 70 to 80 per cent. The weak chamber acid is good enough for a great many industrial purposes and is very cheap. If it is to be concentrated this must be done in vessels of lead up to a certain concentration and then in platinum or gold-lined stills if stronger acid is needed. Naturally this is expensive and every effort was made to find a method of making strong sulfuric acid without the necessity of this intermediate step. Especially was this true when the dyestuffs industry began to demand very large quantities of tremendously strong sulfuric acid which was not only 100 per cent but also contained a considerable amount of sulfur trioxide dissolved in it (fuming sulfuric acid).

The difficulty was overcome by using another catalyst (platinum) in the place of the oxides of nitrogen. If sulfur dioxide and oxygen (air) are passed over the metal the two gases unite to form sulfur trioxide much more rapidly and in the absence of water. Since platinum is very expensive and its action depends on the surface exposed, it is spread on asbestos fibers and

does not look at all like the shiny metal of the jeweler. This method is known as the contact process and the product is sulfur trioxide, which represents the highest possible concentration of sulfuric acid and can be led into ordinary oil of vitriol (98 per cent sulfuric acid) and then diluted with water and brought to 98 per cent acid or left as fuming acid, depending on the requirements of the case. The perfection of this process was the result of some very painstaking research because when it was tried at first it was found that the platinum soon lost its virtue as a catalyst, and it was also discovered that the reason for this was the presence of arsenic in the sulfur dioxide. To get rid of every trace of arsenic is the hardest part of the contact process.

VITRIOL

Next time you visit a laboratory ask to be shown a bottle of concentrated sulfuric acid. You will see a colorless, oily liquid, much heavier than water, as you will notice if you lift the bottle. A little on your skin will raise white weals and then dissolve your body right away; paper is charred by it as by fire. When it touches water there is a hissing.

SULFURIC ACID AND CIVILIZATION

A dreadful oil, but its importance to industry is astonishing. If the art of making it were to be lost tomorrow we should be without steel and all other metals and products of the metallurgical industry; railroads, airplanes, automobiles, telephones, radios, reënforced concrete, all would go because the metals are taken from the earth by using dynamite made with sulfuric acid; and for the same reason construction work of all kinds, road and bridge building, canals, tunnels, and sanitary construction work would cease.

We should have to find other ways to produce purified gasoline and lubricating oil. The textile industry would be crippled. We should find ourselves without accumulators, tin cans, galvanized iron, radio outfits, white paper, quick-acting phosphate fertilizers, celluloid, artificial leather, dyestuffs, a great many medicines, and numberless other things into the making of which this acid enters at some stage.

If at some future date, however, all of our sulfur and all of our sulfur ores are burned up the chemist will yet find ways of making sulfuric acid. Possibly he may tap the enormous deposits of gypsum which exist in all parts of the earth. This has been done to some extent already but is not a process which is cheap enough to compete with sulfuric acid made from sulfur.

Nitric Acid

It is essential that all the heavy chemicals, that is, the most used acids, alkalies, and salts, should be made so far as possible from readily available cheap material. We use air, water, and abundant minerals on this account. Nitric acid caused the chemical industry much concern until it was found possible to make it from air, because until then its source was Chile saltpeter, or sodium nitrate, a mineral occurring in a quantity only in the arid Chilean highlands. However, this source of supply is still the most important and the process used is one of great interest.

Having made oil of vitriol, the chemist found that he could produce other acids, one of the most important of these being liberated from saltpeter by the action of sulfuric acid. When nitric acid is made in this fashion we find that the sulfuric acid is changed into sodium sulfate and remains behind in the still.

One might think from this that sulfuric acid is stronger and on that account that it drives out nitric acid, but in fact this preparation depends on a very simple principle, one of great importance.

ANOTHER DANCE

We may best illustrate it by returning to our former simile. Let us assume a sodium nitrate juggler moving rather slowly. He is bumped into by a sulfuric acid juggler moving at about the same rate. They exchange some of the atoms with which they are playing and in consequence one juggler holds sodium hydrogen sulfate while the other holds nitric acid.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

The nitric acid molecule does not slow down the juggler as much as the sodium hydrogen sulfate and therefore this particular dancer moves away quite fast. Suppose millions of these exchanges to be taking place; then the nitric acid molecules will continue to dance away and will not come back to exchange their atoms any more. If we keep them all in by putting a lid on, then they are forced to go back and we get no more than a sort of game of ball in which the hydrogen and sodium atoms are passed back and forth. If, on the other hand, we open the lid and put a fire under the pot, the nitric acid molecules move faster and sooner or later all of them are driven out.

Nitric acid is now made from the air in more than one way so that we are entirely independent of the beds of Chile saltpeter no matter what might happen to them. Without nitric acid we could not make guncotton, dynamite, TNT, picric acid, ammonium nitrate, and the other explosives which are so enormously im-

portant to our civilization. In addition, we would lose all our brilliant dyes and most of our artificial silk, from which it is easy to see that this substance is of great importance to all of us.

Salt, the Jewel Box

SODA

Among the treasures to which man fell heir as the most important inhabitant of the earth was one of innumerable little cubes made of sodium and chlorine, crystals of salt. These he noticed whenever seawater evaporated and he soon found, if he lived on a vegetable diet as he did in some places, that the addition of these to his food made it much more pleasant and savory. In fact, it is a necessity for the health of the human body. Hunting peoples do not use it so much because they live almost entirely on meat, which contains sufficient salt. Next it was found that salt could be employed for preserving fish and meat, and thus man was able to tide over the periods in which hunting was poor. For ages and ages it was put to no other use. Nobody but a chemist would have thought of doing anything with it. In order to understand the whole of what he did and the part which salt plays in industry owing to the chemist's activity we must go back a little.

SOAP AS A HAIR DYE

Very early it was found that the ashes of a fire (and fires at that time were always made of wood) were useful in removing grease from the hands. They were the earliest form of soap and it is surprising how long they remained the only thing used. Our records go to show that the Romans were the first of the more civilized peoples to find out how to make real soap,

and they learned it from the Gauls, who used the material which they made from wood ashes and goat's tallow for washing their hair and beards because they believed that this gave them the fiery red appearance which they thought was becoming. The Romans saw the advantage of soap over wood ashes and a very considerable trade in the making of various kinds of soaps arose, but the difficulty always was with the production of the ashes because it takes quite a lot of ashes to make even a small quantity of soap. The advantage of having something more abundant to take the place of the ashes was evident. But the real stimulus which led to the discovery of soda ash came from a different source.

GLASS FROM ASHES AND SAND

It was found that ashes heated with sand formed glass. It was also found that the ashes of marine plants, or plants occurring on the seashore, gave a much better glass than that which could be made from the ashes of land plants. In consequence of this, as the art of glass making grew, barilla, the ashes of a plant growing in the salt marshes of Spain, became an increasingly important article of commerce and upon it depended the great glass factories of France and Bohemia. Owing to the political situation which arose at the end of the eighteenth century, France found herself in danger of losing her supremacy in the art of making glass because England cut off her supply of the Spanish ashes. For some reason the French ruler at the time had vision enough to see that it might be possible to make barilla artificially from some source within the kingdom of France and he offered a prize to any one who would make his country independent of Spain. We have seen that the chemist's

business is the transmutation of one kind of material into another, and naturally it was the chemist who came forward with a solution of the problem. Since this process is now supplanted by a more economical one, we will merely outline it here.

LIMESTONE TO WASHING SODA

Remember that it is essential to start from some abundant common material. Le Blanc, the chemist who solved the problem, knew that the Spanish ashes contained sodium carbonate, the formula of which we write as Na_2CO_3; that is, it is a combination of sodium, carbon, and oxygen. There are a great many carbonates in nature and among these is that of calcium which we know as chalk, limestone, or marble, depending on the way in which it crystallizes. In this we have a substance of the formula $CaCO_3$. Suppose, then, we write the two compounds side by side: Na_2CO_3, $CaCO_3$. Evidently the only difference is that in one we have two atoms of sodium (Na_2) in place of one of calcium (Ca) in the other. Salt contains sodium and is very common. If, then, we can get the sodium radical from the sodium chloride and the carbonate radical from the limestone and join the two pieces we will get sodium carbonate, which is what we want. What Le Blanc did was to treat sodium chloride with sulfuric acid. This gave him sodium sulfate and hydrochloric acid. Then he heated the sodium sulfate with coke or charcoal and limestone, after which he extracted the mass with water and found that he had sodium carbonate in solution.

The steps do not sound difficult but it was really a great feat to make them commercially possible. In the first stage when sulfuric acid acted on the salt, hydrochloric acid was given off and this was a great

nuisance. The amount of it produced exceeded any use that could be found for it and it was poured away; being highly acid it undermined the houses in the neighborhood and caused a great deal of trouble. Later, it became the most valuable product of the process because it was converted into bleaching powder by a method that we will take up subsequently.

INDUSTRY A RESULT OF CHEMICAL DISCOVERY

It is interesting to learn that this process which France invented in her extremity became one of the largest industrial developments in England. It caused the flourishing there of the sulfuric acid industry because this acid was necessary for the process and, as we have seen, sulfuric acid is tremendously valuable in a great variety of directions. It also made possible the development of an enormous textile industry because the making of cloth needs soap and bleach, both of which were first supplied in abundance as a consequence of Le Blanc's discovery.

To return to the story of the chemist's transformations of salt, the present process for the conversion of this compound into sodium carbonate is by the action of ammonia and carbon dioxide upon a saturated solution of it, the carbon dioxide being obtained from limestone. When these three substances are brought together a change takes place which can best be described by the following equation:

Ammonia		Water		Carbon Dioxide		Ammonium Bicarbonate
NH_3	+	H_2O	+	CO_2	=	NH_4HCO_3

Salt		Ammonium Bicarbonate		Sodium Bicarbonate		Ammonium Chloride
NaCl	+	NH_4HCO_3	=	$NaHCO_3$	+	NH_4Cl

The change that takes place depends on the fact

that sodium bicarbonate is comparatively insoluble and separates out. It is collected and then heated, the heat causing it to turn into sodium carbonate, carbon dioxide, and water.

$$2\,NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

In this process the essential thing is to keep the ammonia in the system, because it is used over and over again and, if it escapes, an expense arises out of all proportion to the value of the carbonate which must be sold at a price of about two cents per pound. The ammonia goes out of the reaction, as indicated in the equation, in the form of ammonium chloride and this is returned to the process by allowing quicklime, made by heating limestone in kilns, to decompose the chloride. The other part of the limestone (the carbon dioxide) is also used in the process, as shown in the first equation. We start then with salt, water, and limestone, and we finish with calcium chloride and sodium carbonate.

Caustic Soda

This is not all that the chemist was able to do with salt. In soap making much better results are obtained if, instead of using wood ashes which give us nothing but an impure soft potash soap, we use sodium hydroxide or caustic soda. Now, caustic soda is something which does not occur in nature because it always combines with the carbon dioxide of the air or with some acid material and disappears. The old method of making it was to take the soda of the Le Blanc process and to treat it with slaked lime. In this way we can make about a 14 per cent solution of caustic soda which is then evaporated if it is required in a more concentrated form. This method of making

caustic soda was sufficiently economical to give us all that we needed at very reasonable prices, but eventually a better method was discovered.

Caustic soda is NaOH, that is to say, it is water (H_2O) in which one of the hydrogens has been replaced by sodium. If in any way we could make this reaction take place, $NaCl + HOH = NaOH + HCl$, we would get directly two products which we want. Unfortunately, it is impossible to get salt to exchange atoms in this way with water. However, a study of salt solutions showed that the atoms of sodium and chlorine were actually separated when in solution and that they also acquired a property which would allow of their segregation. They became electrically charged and it is always possible to attract an electrically charged body by using a charged body of opposite sign. If, then, we put the positive and the negative pole of a battery or another source of electricity in a solution of salt the chlorine will wander away to the positive and the sodium will wander to the negative pole.

ELECTRONS

What takes place can best be described by a rough analogy. Suppose two automobiles of different makes are running side by side, keeping together because of the friendship which exists between the two parties. Now suppose these two machines have an accident in which, by a freak, one wheel is torn off one car and added to the other. Assume that the occupants of the car are not damaged and that the cars can still run; also that the fifth wheel is a distinct nuisance. If there were two garages at considerable distances, one of which specialized in taking off extra wheels and the other did nothing but put on missing wheels, and the accident were a common one involving thou-

sands of machines, then it would be natural for the cars to move in opposite directions to these two garages and if we assume that all the wheels are interchangeable, then there might be a traffic between the garages, by another road perhaps, the wheels being sent from one to the other.

This very rough picture is intended to describe the fact that when the sodium and chlorine atoms of salt are separated by water the electrons of which they are composed are distributed in such a way that there is an extra one in the chlorine which (an electron being negative) makes the chlorine particle negative, while the sodium lacks one electron and therefore becomes positive since it was neutral before. The result, then, of this electrolysis or use of the electric current in separating the charged atoms of sodium chloride (the ions as they are called) is that sodium and chlorine are given off at the two poles. Now, chlorine is not very soluble in water and can be collected as a gas. The sodium, on the other hand, as each little particle is liberated, reacts with the water about it to give hydrogen and sodium hydroxide. Therefore, we have accomplished what we set out to do, only instead of getting sodium hydroxide and hydrogen chloride we get sodium hydroxide, chlorine, and hydrogen.

ELECTRICITY

The success of this method is due to discoveries in another field of science. Only when Michael Faraday's researches on the nature of the electric current made available another source of energy different from heat, was it possible for the chemist to carry out what has just been described; at first only in a very small way but, as the production of electricity became more

and more economical, ever on a larger scale until now the industry is a most important one.

Chlorine

So far we have directed our attention almost entirely to the sodium atom of salt; the other part of the molecule, the chlorine, is also extremely valuable to us. It used to be set free by oxidizing the hydrochloric acid of the Le Blanc process with manganese dioxide. Now, as we have just seen, we get it directly from a solution of salt by electrolysis.

Uses of caustic soda

The two servants which the chemist has conjured out of salt by using electricity are extremely valuable, though if they are not handled rightly they are equally as dangerous as they are useful when put to work. Caustic soda is a white, waxy-looking solid which is extremely soluble in water and attracts moisture from the air. It is highly corrosive, destroying the skin and attacking a great many substances. When it is allowed to act on cellulose in the form of cotton the fiber undergoes a change which results in its acquiring greater luster so that the process of mercerizing, as it is called, is valuable industrially. The manufacture of artificial silk made by the viscose method depends on the fact that caustic soda forms a compound with cellulose. Practically all the soap manufactured at the present time is produced by the action of caustic soda on fat. The by-product of this industry is glycerol which is used in making dynamite. In fact, soda is just as important among alkalies as sulfuric acid is among acids.

USES OF CHLORINE

Chlorine, the partner of sodium, is a frightfully destructive material. It attacks organic substances of all kinds, destroying them completely, and it also attacks all metals, even platinum and gold, though fortunately, if it is quite dry, it does not react with iron, and on that account it can be stored under pressure in iron cylinders. Although it is such a deadly gas if allowed to run wild, yet it is extremely useful and its discovery has been very greatly to the advantage of the human race. First of all, it is employed in the manufacture of bleaching powder, a product which enables the cotton industry to work far more intensively than it otherwise could. Formerly cotton was bleached by laying it on the grass, but that is much too slow for our present mode of life. In fact, we have no room for it because it has been calculated that the cotton output of Manchester, England, would require the whole county as a bleaching field and this is obviously impossible. Then came the discovery that this same compound could be used in purifying our water supplies of dangerous disease-breeding bacteria and this has reduced the typhoid death date from that of a very dangerous epidemic disease to a negligible figure. Now, whenever the water supply of a city is questionable, chlorine is pumped right into the mains or else a solution made from bleaching powder is used. Twenty parts of bleaching powder per million is sufficient to kill 90 to 95 per cent of all the bacteria in the water. For medical use, a solution of hypochlorous acid, which is the active principle of bleaching powder, has been developed into a marvelous treatment for deep-seated wounds, and recoveries which formerly would have been out of the question

are now possible. Chlorine is also used in very large amounts in making organic chemicals which the public enjoys as dyestuffs or sometimes does not enjoy as pharmaceuticals or medicines.

All in all, the products obtained from the little salt cube are of extreme necessity and importance to everyone of us and their utilization shows what can be done when men of genius devote themselves to the acquisition of real knowledge and then translate their discoveries into commercial enterprises for the benefit of humanity.

Chemistry and Understanding

The brief story for which we have space indicates but very dimly the real interest and fascination the chemist has in handling matter. His knowledge has increased to such a point that he can build you a molecule almost to order to meet any specifications. To be without any knowledge of chemistry is to go through life ignorant of some of the most interesting aspects of one's surroundings; and yet the acquisition of some knowledge of this subject is by no means hard. There are any number of books which tell the story in simple language if you do not wish to study the science intensively. On the other hand, all that you need is a real interest and a willingness to think as you read.

CHAPTER II

ABRASIVES

F. J. Tone

President, The Carborundum Company

Modern chemistry has revolutionized the art of shaping and finishing metals by grinding. By the creation of the artificial abrasive the chemist has profoundly influenced present-day mechanical methods. Shaping edged tools and metal implements by the use of naturally occurring stones and hard rock fragments has been practiced from most ancient times. Emery, which is impure aluminium oxide, was used for grinding and polishing in the time of the Pharaohs. The ancient Indians used it for polishing stones and from these historic times down to the discovery of carborundum by Acheson, it constituted the most efficient abrasive for the mechanical arts. In 1891, Acheson, who had long been impressed with the possibility of replacing emery by a harder material, conceived the idea of using the electric furnace to produce a form of crystalline carbon which would possess some of the properties of the diamond and be useful as an abrasive. He recognized that carbon was the hardening agent in steel and that carbon in its crystal form as diamond was the hardest known substance. He decided, therefore, to make experiments on impregnating clay with carbon under the influence of electric heat. This was the first conception of an artificial

abrasive and his autobiography gives the following narrative of his first experiment:

> An iron bowl, such as plumbers use for holding their melted solder, was attached to one lead from a dynamo and filled with a mixture of clay and powdered coke; the end of an arc light carbon attached to the other lead was inserted into the mixture. The percentage of coke was high enough to carry a current, and a good strong one was passed through the mixture between the lamp carbon and bowl until the clay in the center was melted and heated to a very high temperature. When cold, the mass was examined. It did not fill my expectations, but I, by sheer chance, happened to notice a few bright specks on the end of the arc carbon that had been in the mixture. I placed one on the end of a lead pencil and drew it across a pane of glass. It cut the glass like a diamond. I repeated the experiment, and collected enough of the material to test its abrasive qualities. I mounted an iron disc in a lathe, and, oiling its surface, applied the material which adhered, and with this revolving disc I cut the polished face off the diamond in a finger ring still owned and worn by me.
>
> I now made a small furnace of bricks, and after much and patient work, had what I considered enough to take to the lapidaries in New York City. On the way I coined a name for my new and, as yet, unnamed material. Under the impression, without any chemical analysis, that it was composed of carbon and corundum, I called it Carborundum.

Thus keen observation of an experiment which many would have called a failure led to a great discovery. The small iron pot was the cradle of the artificial abrasive and the beginning of an industry now having an annual production of thirty thousand tons. The iridescent crystals were in due time isolated as silicon carbide, a heretofore unknown chemical compound, the molecule consisting of one atom of silicon and one atom of carbon. Carborundum is today made in enor-

mous quantities by the reaction of carbon and sand at the high temperature of the electric furnace. The reaction is expressed by the following equation:

$$SiO_2 + 3C = SiC + 2CO$$

This is the reaction of the carborundum furnace in its simplest form but more complicated reactions undoubtedly occur. Silicon carbide does not form from a liquid nor can it be melted after formation. If one attempts to melt silicon carbide, the crystal decomposes. Vapor of silicon metal goes off and leaves graphite in the form of the original silicon carbide crystal, i.e., a graphite pseudomorph of the carborundum. These facts led to the conclusion that silicon carbide is formed principally from gaseous constituents. Vapors of carbon may be present in the furnace but not in sufficient quantity to account for the main reactions. In the atmosphere of the furnace we have large quantities of carbon monoxide, vapors of silicon dioxide, and the element silicon. These gases are formed by the interaction of the sand and coke, probably by the reaction:

$$SiO_2 \text{ (solid)} + 2C \text{ (solid)} = Si\text{(gas)} + 2CO \text{ (gas)}$$

Then follows the reaction:

$$3Si \text{ (gas)} + 2CO \text{ (gas)} = 2SiC + SiO_2$$

Thus the crystals of silicon carbide are built up directly from gases.

Chemistry of High Temperatures

This synthesis of silicon and carbon by Acheson was typical of the new chemistry of high temperatures.

The refractory oxide, silica, constituting more than one-half the earth's crust had up to that time been one of the most difficult substances to reduce. Under the heat of the electric arc, molecular bonds were loosened and new affinities were disclosed. Silica readily parted with its oxygen and formed new compounds. Previous to the advent of the electric furnace the highest temperature commercially available to the chemist was about 1800° Centigrade. The electric furnace at once raised this limit to 3500° Centigrade, the temperature of carbon vapor in the carbon arc. Elements and compounds which were inert at temperatures formerly obtainable were now seen to be capable of great chemical activity and the temperatures made possible have given the world not only carborundum but a long list of useful high-temperature products including calcium carbide, metallic silicon, cyanamide, graphite, phosphorus, nitric acid, ferrosilicon, ferrochromium, and other ferro-alloys which have so fundamentally affected the metallurgy of steel. It was most opportune that just at the time when the electrochemist was making available to the world these new elements and compounds by means of the electric furnace and the electrolytic cell, requiring large amounts of cheap electrical power, the hydro-electric engineer solved the problem of harnessing large waterfalls. Niagara and the other early power installations were thus made commercially successful because the electrochemist had created a large market for electric power. Neither could have had such immediate success without the other.

The first carborundum furnace produced one-quarter of a pound a day, the production being taken by jewelers and lapidaries at a price of eighty dollars per

pound. The present-day furnaces consume 3000 horsepower and produce 16,000 pounds in 36 hours with a market value of about 15 cents per pound. The furnace mixture consists of silica in the form of very pure glass sand and carbon in the form of finely ground petroleum coke, a residue of the oil refineries. To these are added varying amounts of sawdust and common salt. The sawdust is used to make the mixture porous so that the large amounts of carbon monoxide gas may escape evenly through the charge. The salt forms chlorides with the impurities present in the coke and sand and assists in their elimination. A typical furnace mixture consists of sand, 56 per cent; coke, 35 per cent; sawdust, 7 per cent; and salt, 2 per cent.

Electric Furnaces

Electric furnaces are classified under three general types: the resistance furnace; the arc furnace; and the induction furnace. The carborundum furnace is of the resistance type; that is to say, the electric energy is converted into heat by passing it directly through an electrically resisting material. It consists of a rectangular brick structure 45 feet long, 10 feet wide, and 10 feet high. The ends of the furnace are permanent and enclose the carbon electrodes which carry the electric current into the furnace. The outer ends are connected with the source of electric energy. In preparing the furnace for a run, the interior is first filled about half full with the mixture of coke, sand, salt, and sawdust, and a trench 3 feet wide and 1 foot deep is formed from end to end and is filled with granular coke. This core serves to connect the electrodes and forms the conductor for the current consti-

tuting the resistor. The furnace is then filled with the mixture over and completely surrounding the core and is ready to operate. Power is turned on and the current of 10,000 amperes traversing the core is converted into heat, quite like the heating of the filament of an incandescent lamp but on a tremendously greater scale. This heat is transferred to the surrounding mixture and rapidly brings it to the high temperature where the reaction between silica and carbon is accomplished. The range of reaction temperatures is from 1500° to 2200° Centigrade. The furnace is operated for 36 hours, and after cooling the side walls are torn down and the outside layer of uncombined mixture is removed, exposing the cylindrical mass of sharp, brilliant crystals. These are unloaded in the form of large lumps of loosely adhering crystals and are delivered to the crushing plant for the various processes of crushing, refining, and sizing.

Artificial Graphite

As a direct result of the production of carborundum came also Acheson's discovery of artificial graphite. He found that when the furnace temperature was carried to 2240° Centigrade, or beyond the formation point of silicon carbide, the molecule broke up, the silicon going off as vapor and the carbon remaining in the form of graphite. On this principle of the decomposition of carbides to graphite is based the artificial graphite industry.

The discovery of carborundum stimulated research in the production of other artificial abrasives, and in 1899 Charles B. Jacobs invented a process for making crystalline alumina or artificial corundum in the electric furnace by the fusion of bauxite. Bauxite is the

purest form of aluminium oxide found in nature in commercial quantities and includes as its principal impurities silica and oxides of titanium and iron. In the manufacture of abrasives the bauxite is first calcined to remove about 30 per cent of water and then mixed with ground coke and iron borings. This mixture is introduced into a circular furnace of the arc type consisting of a steel shell about 7½ feet in diameter and 6 feet high, the bottom being lined with carbon. This shell, constituting the sides of the furnace, is water cooled and requires no lining. The top of the furnace is open. The electrodes are suspended vertically into the furnace, and as the mixture is fed in and fused the ingot is gradually built up. When the furnace is filled, the power is shut off and the ingot is allowed to cool and solidify. The alumina has been found to be converted into a crystalline material of great toughness and hardness analyzing about 96 per cent alumina. The impurities for the most part have been reduced and combined with the iron to form silicides of iron and titanium, useful as low-grade ferrosilicon. This alloy settles to the bottom of the furnace and is easily separated.

Artificial corundum has been given various trade names, such as alundum and aloxite. In chemical composition it is similar to ruby and sapphire and not radically different from natural corundum, but it differs in physical structure, as the alumina crystals are bound together by a thin matrix of the impurities, thus giving it in higher degree the properties of hardness, toughness, and uniformity which are required in an abrasive suitable for a grinding wheel. The artificial product is now superior to the natural, another instance where the chemist has improved upon Nature.

When the crude abrasive leaves the furnace room it is delivered to the crushing plant for conversion into abrasive grains and powders. It is crushed through heavy rolls and then subjected to refining by washing, chemical treatment, and magnetic concentration to remove impurities. The chemical treatment of carborundum consists in boiling it in sulfuric acid and then in a solution of caustic soda. This removes graphite, silicon, and silicides of iron and aluminium. The abrasive is then sized by screens and classifiers to give a long range of sizes from No. 6 mesh down to the finest powders. In this grain form it is ready for use for the polishing of metal or stone, or for further fabrication into grinding wheels, abrasive paper, and cloth, sharpening stones, and the like.

Grinding Wheels

The making of the abrasive into wheels and other shapes is again the work of the chemist. The wheel is composed of two principal components—the abrasive grains and the bond that holds them together. Various materials are used as bonds, the principal ones being porcelain, silicate of soda, shellac, rubber, and the phenol resins, bakelite and redmanol. The porcelain-bonded wheel made by what is termed the vitrified process is most widely used and has presented to the ceramic chemist a long line of problems which have been most successfully solved. The first requirement is the accurate regulation of the grade of the wheel to meet successfully the wide range of grinding work. Grinding wheels must be made in various grades, that is, various degrees of hardness; for example, for grinding steel castings an entirely different grade is required from that for grinding tempered

steel. This variation in grade is obtained by varying the amount and character of the bond used and by the subsequent heat treatment or burning in the kiln. These operations require the closest scientific control in order that every wheel of a given grade and every portion of the wheel shall duplicate the grade standard. Moreover, the grinding wheel revolves at a peripheral speed of a mile a minute, and in addition to the high centrifugal stresses from this high speed, it must stand severe impact and tortional stresses from heavy castings and metal parts which are being ground—certainly a hard requirement for a mere piece of pottery. Among all ceramic articles, therefore, the vitrified grinding wheel may be regarded from mechanical considerations as the highest achievement of the ceramic chemist.

In making the vitrified grinding wheel the abrasive grains are first mixed with clay, feldspar, flint, or other ceramic materials, and molded to shape by pressing or puddling. The shapes are then fired in kilns to a temperature of about 1300° Centigrade for a period of four to five days, thus vitrifying the clay-bonding material. After removal from the kiln, the wheels are trued up in a lathe, bushed with lead in the arbor hole, and subjected to speed tests. They are then ready for use.

Organic chemistry has contributed its important part to the abrasive art in the making of the so-called elastic grinding wheels which are bonded with rubber, bakelite, redmanol, or the like. In the sawing of granite, marble, and carbon, and the cutting of tool steel, stellite, and various materials which cannot be cut with metal saws, there is required an abrasive wheel extremely thin and of great toughness and elasticity.

For this purpose the elastic grinding wheel made with an organic bond has proved most efficient.

Applications

To describe the work of the artificial abrasive in the industries would be to enumerate almost every product of the manufacturing arts. In the metal industries it ranges from victrola needles to locomotives, from fountain pens to plows and harvesters; in the stone industries it has revolutionized the working of marble, granite, and onyx; it is indispensable in the finishing of fine leather and shoes; it surfaces and bevels glass; it shapes pearl buttons and precious stones. The Chinese use large quantities of carborundum for polishing jade. The East Indians make carborundum wheels for hulling rice. Shackleton carried a carborundum sharpening stone to the Antarctic and described it as indispensable. On ocean steamships carborundum crystal receivers are much used in radio communication.

Our present-day standards of living have been brought about largely through the products made available by what is called quantity production. In the mechanical arts quantity production is founded on the principle of turning out a vast number of parts which are exact duplicates, the one of the other, and which can be assembled interchangeably. The big contribution of abrasives to quantity production is the precision grinding machine and grinding wheel. This machine is unique in that it combines quantity production with the utmost refinement and accuracy. Thousands of machine parts can be produced, each one varying from the other not more than a fraction of a thousandth of an inch. On hardened steel where the

lathe fails altogether, the precision grinder has made possible the use of hardened steel crank pins, spindles, and wearing parts in machines of every variety. It has given perfect accuracy in bearing parts, and this means a permanent oil film in lubrication. The retention of the oil film means low friction and long life.

The manufacture of steel balls for ball bearings illustrates the highest accuracy attained in the mechanical arts in quantity production. One carborundum wheel will finish in ten hours fifty thousand steel balls one-quarter of an inch in diameter within limits of accuracy almost unbelievable. The manufacturing limit is one-half of one ten-thousandth of an inch, but certain manufacturers keep this limit well down to one-fourth of one ten-thousandth of an inch, or, popularly speaking, one-fortieth of a hair's breadth.

The mechanical perfection of the automobile and the interchangeability of its parts have been made possible by the modern grinding wheel. Practically every part of the automobile must be ground with artificial abrasives at some stage of its manufacture. Take away from the automobile industry artificial abrasives and the other products which the chemist has made available to it by the electric furnace, such as aluminium, alloy steel, and high speed steel, and the labor cost of building a car would become prohibitive. The industry would cease to exist on its present lines.

A growing field for abrasives is in the construction of nonslipping walking surfaces to safeguard the footsteps of pedestrians. The hazard of slippery floors is one that is little appreciated. Statistics show that the total number of accidents from slipping, tripping, and falling is greater than those caused from automobiles, street cars, and fires combined. Abrasive

grains are now incorporated in floor surfaces such as tile, terrazzo, or concrete, the amount of projecting grains being proportioned to give a slip-proof surface imparting to the step a sense of security without retardation. This is of particular value in stairways, elevator entrances, machinery floors, ramps, hospitals, schools, and railway platforms.

The artificial abrasives have valuable refractory or heat-resisting properties, as might be predicted from the highly refractory properties of the ores from which they are made and from the extreme temperatures at which they are formed. They are used in making bricks and linings for furnaces where extreme heats are maintained or where high heat conductivity or great mechanical strength is required. They are classed with the super-refractories and have a wide application where ordinary fire bricks have failed.

Work to Be Done

What can the chemist of the future accomplish for the abrasive art? The moderate increase of working temperature in the electric furnace gave the chemist a new tool and enabled Acheson and others to reap a rich harvest of experimental results, but the limits are by no means set by present accomplishments. By carrying out reactions under increased pressures in closed receptacles it is possible to control vapor phases, and thus a new set of transformations may be opened up—a new chemistry based on the combination of high temperatures and high pressures. Moissan long since succeeded in making miniature diamonds by suddenly cooling molten iron which was saturated with carbon. Under the great pressures induced by the contraction of the iron, the carbon on solidifying was forced to

assume the crystalline form. He likewise heated sugar in a closed bomb, creating great pressure by means of the gases generated. Upon sudden cooling he obtained the carbon crystals or diamonds. When carbon is heated at atmospheric pressure it has no liquid phase. It passes directly from solid to vapor. Heated under high pressure it has a liquid phase, and the production of diamonds in commercial quantities may find its solution in constructing apparatus thus to bring carbon to its liquid phase and then suddenly cool it. Whatever might be the effect of such a discovery on the gem industry, it would certainly add a useful element in the abrasive art.

Garnet, a natural crystalline mineral, is the most successful abrasive for finishing wood and has never been displaced by the artificial abrasive although it is inferior in hardness. It is used principally in the form of coated paper and cloth, and owes its superiority to its peculiar fracture which gives grains having a chisel-like, cutting edge. The electrochemist has so far been unable to produce an artificial product having these properties. If a substance having a similar structure and greater hardness can be made, it will have great value in the woodworking trade.

Various carbides, such as boron carbide, tungsten carbide, titanium carbide, and zirconium carbide have been studied and are known to possess hardness and other properties surpassing silicon carbide, and if their cost of production can be brought down valuable applications may be developed for them.

Altogether the abrasive field still presents ample scope for creative work on the part of the chemist.

CHAPTER III

ALCOHOL AND SOME OTHER SOLVENTS

D. B. Keyes

Research Laboratory, U. S. Industrial Alcohol Company

Introduction

Everyone knows what alcohol is, but the term solvent is not so clearly understood. A solvent may be considered to be a liquid which will form a uniform fluid mixture with some other substance. The importance of solvents is not appreciated by the public, nevertheless none of our great industries would be possible if it were not for this class of substances. In fact, life itself would not exist without them.

When water dissolves sugar, we call the resulting mixture a solution of sugar in water and we speak of water as the solvent. The sugar undergoes a change when it dissolves in the water. It becomes so finely divided that the particles are no longer visible to the eye. In this finely divided condition it is reactive and can be made to undergo chemical change. This is the reason for the importance of solvents. All industries depend upon chemical reactions and these reactions take place more readily in solution, which, in turn, is due to the fine state of subdivision of the dissolved substances.

Water is our greatest solvent. Its uses are unlimited and it is very fortunate for us that the supply is adequate for our needs. Alcohol, which resembles water in many ways, is next in importance. There are

a number of other liquid solvents that are useful in our industries, and this number will increase until we have a solvent to meet every particular need.

Alcohols in General

Alcohols are many in number though there are only two common ones at the present time, methyl alcohol (methanol or wood alcohol, CH_3OH) and ethyl alcohol (alcohol, C_2H_5OH). As can be seen, these compounds are characterized by the hydroxyl groups (OH) and an alkyl group consisting of carbon and hydrogen (example, C_2H_5).

Besides this particular series, which includes the higher alcohols such as butyl alcohol (C_4H_9OH) and amyl alcohol ($C_5H_{11}OH$), there are other series which contain more than one hydroxyl group. Glycerol,

$$\begin{array}{l} CH_2-OH \\ | \\ CH\ -OH \\ | \\ CH_2-OH \end{array}$$

is an alcohol containing three hydroxyl groups and, as would be expected, glycerol is a good solvent. Still other alcohols are the aromatic alcohols, such as phenol (carbolic acid, C_6H_5OH), which have acid properties and are characterized by the fact that the carbon and hydrogen group contains a so-called benzene ring; they come from coal tar. These also may have more than one hydroxyl group. Still other more complex alcohols are known but are used in comparatively small quantities.

Ethyl Alcohol

Ethyl alcohol (C_2H_5OH) goes under several different names—alcohol, grain alcohol, industrial alcohol,

and molasses alcohol. It is made by the fermentation of sugars, and is a colorless, sweet-smelling liquid boiling at 78° Centigrade.

MANUFACTURE

In this connection sugar-cane molasses is the chief source of alcohol; corn is next in importance. Germany uses potatoes, France uses sugar beets, and other countries have found sorghum valuable. Attempts have been made not only to use sugars and starch (converted into sugars) but also cellulose (wood). The wood is treated with acid and converted into molasses. Engineering difficulties have prevented this process from being economical at the present time. It can be easily seen that ethyl alcohol can be made from nearly every form of plant life and because molasses has a limited production some other satisfactory raw material must be found before alcohol will be produced in quantities necessary to meet the needs of the United States.

Waste materials have been investigated by many, but this seems to be a poor way to attack the problem. The future development of alcohol manufacture will probably be the use of some rank tropical growth that contains high percentages of starch and sugar. Alcohol has been made from many tropical plants but this is not the important feature. Alcohol must be made from these plants by a process that is based on sound engineering and economic principles. This means that no amateur chemist or eccentric inventor will discover the satisfactory solution. They may contribute their bit, but the process will finally be worked out in the usual long, painstaking way by a group of highly trained scientific men, business men, and engi-

neers. It will come, but no one genius will discover it overnight.

Yeast, a living organism, reacts on sugar, producing alcohol and carbon dioxide gas. The equation may be written as follows:

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

This reaction takes place in bread when yeast is used to make the bread rise; in fact, it is an extremely common reaction because sugars and yeast occur over a wide range in nature.

Molasses from the sugar mills of Cuba is transported in tank steamers, similar to oil tankers, to the North Atlantic Coast and pumped into storage tanks. The molasses, diluted with water and a little acid in order to give the yeast better working conditions, is taken into the alcohol plant. The yeast, grown in a pure medium free from bacterial contamination, is added and the fermentation continues for about three days. The carbon dioxide comes off and is collected, purified, and stored in cylinders to be sold for use at soda fountains. The resulting mash contains from 6 to 10 per cent of alcohol and resembles that obsolete beverage, real beer.

The mash is pumped into a still and the alcohol separated from the slop by distillation with steam. As the original molasses contains many substances besides sugar, it is no wonder that many impurities distil over with the alcohol. These impurities are aldehydes, esters, and higher alcohols. They do not decrease the solvent powers of the alcohol but they impart a distinct odor which is objectionable in certain cases. It, therefore, is necessary to rectify this crude alcohol. Rectification is a simple process of auto-

matically redistilling a solution many times, using only one still. This scheme of purification has been developed to a high state and alcohol is one of the purest chemicals sold.

Not all of the troubles of the alcohol manufacturer are technical, for the industry is circumscribed by many legal regulations.

BY-PRODUCTS

The purified carbon dioxide gas obtained from the fermenting tubs is compressed into steel cylinders and used not only for making soda waters and for carbonating soft drinks but also as a preservative. Butter and ice cream are churned with carbon dioxide, which improves their keeping qualities and also swells the volume so the customer may think he is getting more for his money; he is, but it is only gas. Cookies, crackers, and biscuits are sent abroad in air-tight tin cans. These cans have the free space filled with carbon dioxide.

The residue from the stills after the alcohol is distilled off is called distillery slop. This material is concentrated to a thick sirup and then burned in a furnace. The ash contains about 35 per cent potash (K_2O) and is a valuable fertilizer material. The gases coming from this furnace are washed with water in order to recover ammonia, another well-known chemical which has many uses but may be considered chiefly as a plant food or a fertilizer for the soil.

Several other valuable chemicals are contained in the slop but only in small quantities. To get out these constituents would take more money, using present methods, than they are worth. This problem resembles the problem of obtaining gold from sea water.

Glycerol, however, occurs in appreciable quantities and brains and money are all that are necessary to to make this recovery an economic success. One concern in the United States loses one thousand dollars worth of glycerol a day in this manner.

In the refining of alcohol by distillation two fractions are withdrawn as impurities. One contains higher boiling alcohols, such as propyl, butyl, and amyl alcohols. The other contains a mixture of aldehydes. Amyl alcohol (fusel oil) has been in great demand for many years as a high-boiling solvent in nitrocellulose plastics, films, and lacquers. This product is collected and saved, not only in this country but in all of the European countries. There is not nearly enough to meet the demand in the United States and many processes have been devised to increase the yield in fermentation and also by direct chemical manufacture. These efforts have been unsuccessful. In fermentation it seems to be made not from the sugar but from certain nitrogen bodies that are put in as yeast food. These bodies are not clearly defined and as yet no satisfactory raw material has been found. This appears to be a productive field for future research.

The butyl alcohol (isobutyl alcohol) found in fusel oil has been found to be an excellent solvent for many substances, but the source of supply is limited. Artificial musk, a constituent of the finest perfumes, is made from this alcohol.

The propyl alcohol (normal propyl alcohol) is a good solvent, but so closely resembles ethyl alcohol that its development is not worth while.

The aldehydes mentioned are too reactive to be used as solvents and they have a disagreeable, penetrating odor. There should be some good use for these sub-

stances, and it will not be long before some chemist will put them to work.

Uses of Ethyl Alcohol

Ethyl alcohol or, as it is known in the trade, industrial alcohol, has more uses than practically any other chemical, except sulfuric acid and caustic. Water is the only solvent that is used in greater quantities than alcohol. It might be said that water and alcohol nine hundred and ninety-nine times out of a thousand will answer all the chemist's needs when he desires a solvent.

Nearly all alcohol used for industrial purposes is first denatured in order to render it unfit for beverage purposes. This alcohol is not taxed by the Government. There are over a hundred different denaturants. Special ones are selected for special industries, depending upon the use to which the alcohol is to be put. Much of this denatured alcohol is used subject to governmental regulations.

IN THE HOME

Ethyl alcohol has been used and will be used in vast quantities in the home, not only directly but indirectly; for example, denatured alcohol is used for cleaning purposes and as a constituent of metal, furniture, and shoe polishes.

CANNED HEAT

Canned heat, or solid alcohol, is familiar to all and its value as a convenient source of heat is recognized. In this country we do not use alcohol to any great extent for lighting purposes, but in other countries it is being used very effectively. Employing an

ordinary gas mantle, it has been found that alcohol will give out three and one-half times as much candle power as kerosene. Filaments in our modern electric light bulbs have been made by a process which involves the use of alcohol.

PAINT AND VARNISH

Varnishes, lacquers, shellacs, and enamels used around the house all have alcohol as their base. Furniture manufacturers are turning away from the old-time varnish, which required so long a period to dry between coats, to the modern wood lacquers; the solvent is alcohol. Wood lacquer is shot on to the furniture by means of a gun (air pressure) and dries almost instantly. Oftentimes the lacquer can be put on so that no rubbing or polishing is necessary in order to obtain a brilliant finish. The durability of this covering is far ahead of the old-time varnish. Less labor means a marked decreased cost in operation. In other words, cheaper but better furniture.

Shellac, which has the greatest sale of all varnish gums, owes its popularity to its toughness and solubility in alcohol. The so-called spirit or alcohol varnishes are sought mainly because of their ease of application.

As the sale of paint increases, so does the sale of paint removers. In recent years, paint and varnish removers have become a small industry all by themselves. Alcohol is one of the principal constituents of all these solutions.

PYROXYLIN ARTICLES

The pyroxylin or nitrocellulose industry uses enormous quantities of alcohol and the products are so

numerous and so varied that it is probable every home in the United States has some article in it that contains pyroxylin. Pyroxylin is merely a plastic composition containing nitrocellulose or guncotton. This substance, made up into various articles, is sold under the trade names celluloid, pyralin, etc. Examples of what can be made from it are brushes, combs, buttons, mirrors, billiard balls, hat stiffeners, dress ornaments, shoe caps, salt cellars, napkin rings, pin trays, vanity boxes, and a million other things.

FOODS

In the food line, alcohol is used in all the flavoring extracts such as vanilla, ginger, and lemon extracts. A great many attempts have been made to substitute something else for the alcohol in flavoring extracts because of the nuisance of government regulations involving the use of alcohol. These attempts have all been failures.

White vinegar is pure acetic acid and is made by the fermentation of dilute alcohol. Wooden tanks, holding many thousands of gallons, are filled with beech shavings, upon which the bacillus sits while he ties up the oxygen in the air with the alcohol in order to synthesize acetic acid. The alcohol is fed in at the top of the wooden tanks, passing down over the beech shavings, meeting the bacilli together with the air coming up from the bottom. This product is not only sold in tank cars for the manufacture of vinegar but is also sold to commercial concerns wherever dilute acetic acid can be used.

Jellies are often colored with dyes made from alcohol; stick candy is lacquered with a special edible or harmless resin dissolved in alcohol. Pectin, the

substance which housewives now use extensively to make jellies, is recovered from fruits by means of alcohol. Food preservatives, such as sodium benzoate, are made with alcohol. Even the beautiful color of oranges is sometimes brought about by exposing them to ethylene gas made from alcohol.

PHARMACEUTICALS

The druggist probably dispenses more alcohol than any other chemical compound. From cheap perfumes with a powerful, pungent odor to those with the most delicate scent, all contain alcohol. Practically every kind of cosmetic or lotion, liquid soap, shaving cream, tooth paste, mouth wash, hair tonic, germicide, insect exterminator, deodorant, and collodion solutions, all contain alcohol. In recent years special ethyl alcohol solutions so fixed that they are not fit for beverage purposes have appeared on the market as a massage. The invigorating stimulating effects of the old-time grain alcohol are all present in the new rubbing alcohols.

MEDICINES

Perhaps the most vital use of alcohol is in medicine. Over four thousand different medicines require alcohol in their preparation. The list includes such famous drugs as antipyrin, salvarsan, and insulin. If ethyl alcohol had no other use than for the manufacture of these three drugs it would still play a very vital part among the essential raw materials of the world.

There are many other things around the home in the manufacture of which alcohol is required. A few examples are linoleum, gas mantles, inks, paper, pencils,

glues, mucilage, paints, pastes, steel pens, and rubber goods.

ANTIFREEZE FOR AUTOMOBILES

Denatured ethyl alcohol is recognized now throughout the United States as the only safe and efficient antifreeze for automobiles in winter. Tests on all kinds of chemicals for this purpose have been conducted for many years and the conclusion is that alcohol is the only satisfactory product. Millions of gallons of alcohol are sold every winter for this one purpose. The alcohol lowers the freezing point of the water and, at the same time, has no corrosive effect upon the tin, copper, iron, or rubber of the radiators.

ARTIFICIAL LEATHER FOR AUTOMOBILES

So-called artificial leather, which is not artificial leather at all but a textile material that has wonderful wearing qualities, has reached enormous production in recent years. This durable textile material that is now used on practically all of our automobiles where leather was used before is made from nitrated cotton and alcohol. It was formerly only used to cover the cushions and top, but now the entire body of the automobile is often covered with this impregnated textile.

AUTOMOBILE FINISHES

The substitution of lacquers for varnish has been particularly successful in the automobile industry. Varnishes would not endure for long the drastic conditions imposed upon them when placed on the body of an automobile. A nitrocellulose lacquer on the other

hand has no difficulty in retaining its polish and smooth surface under the most severe weather or artificial conditions. It is reasonable to suppose that lacquer will ultimately displace all of the varnishes used for automobile work. Labor and time are the two big items in the cost of automobile construction. Any saving of either will be appreciated by the automobile manufacturer, especially if the resulting car looks better and lasts longer than with old-time finishes.

MOTOR FUELS

Geologists tell us that we are fast approaching a limit to our gasoline supply. A great amount of thought has been spent on discovering some practical fuel with which we can increase our waning supply of gasoline. The concensus of opinion is that alcohol is the best possibility. For the past seven years one alcohol producer has employed a large group of research chemists to work on the problem of producing, among other things, a fuel consisting of gasoline and alcohol which can be easily and cheaply made and which will be superior to gasoline in engine performance and economically sound. Such a fuel has been devised. It has been tested by the United States Navy and the United States Post Office Department as an airplane fuel, and also by other large organizations as a general motor fuel. Results of these tests so far have been satisfactory. The fuel apparently eliminates all tendency to detonate or knock. This means longer engine life, decreased maintenance, greater fuel and oil economy, better lubrication, and more power. No carburetor change is necessary and the fuel mixes in all proportions with gasoline. The Shenandoah, famous dirigible of the United States Navy,

has used this fuel with apparent satisfaction for some time. Airplane races using this fuel broke international records and its performance in automobiles is everything that could be desired. It should be remembered, however, that other sources of alcohol besides molasses must be developed before this fuel can be universally used in this country.

Still another motor fuel made from alcohol has recently been put upon the market. This consists of a mixture of gasoline and tetraethyl lead. The latter removes the knock from the engine and causes the fuel to be burned much more efficiently. This compound, though still in the experimental stage, shows great promise and because only very small quantities of tetraethyl lead have to be used it is believed that the fuel is economically sound.

There are many other products sold by garages which contain alcohol or in whose manufacture alcohol has been used; for example, carbon removers, primers, polishes, and even the rubber tires.

IN WAR

An alcohol plant is a potential munitions plant. In the construction of a 12-inch shell nearly a barrel of alcohol is used. Trinitrotoluol, cordite, and smokeless powder all require alcohol in their manufacture. Once a country has adopted a high explosive all of its artillery and firearms are designed and so constructed as to use only this one explosive. During the World War, England had standardized on cordite and it was necessary to have vast quantities of acetone to gelatinize this product. The acetone production in the entire world is rather small, so new synthetic methods for manufacturing had to be developed. Among the

methods was the transformation of alcohol to acetic acid, acetic acid to calcium acetate, and calcium acetate to acetone. This process was actually operated during the World War, in spite of the high cost of production, because cordite was standardized and any variation in the solvent would have ruined the British artillery and rifles as far as accuracy was concerned.

Airplane wings made of cloth were impregnated with a material called "dope" which was prepared from a nitrocellulose or cellulose acetate solution and alcohol. One of the ingenious inventions of the war was a glass that would not splinter when broken, which could be used in goggles. This product is made by cementing together several layers of glass. Between each glass plate is a film of nitrocellulose made by the use of alcohol.

The percussion cap contains a very unstable compound called fulminate, which will give a pronounced flash whenever set off by a sharp blow. Mercury fulminate is the common one, but many others were tried. All of them required alcohol in their manufacture.

At the end of the World War 60 per cent of the shells fired contained some poisonous gas and in the next war every shell will contain poisonous gas. Alcohol is the base for many of these gases, especially the tear gases and mustard gas. Mustard gas perhaps was the most effective gas used in the late war. This material was made by the action of sulfur chloride on ethylene. Ethylene is a dehydration product of ethyl alcohol. General Pershing asked for the production of a thousand tons per day of mustard gas, and it is reasonable to suppose that the next war will see not only this gas but others similar and more deadly. These will be made in quantities undreamed of at this time.

Alcohol in time of war was as necessary as steel. The establishment of an alcohol industry in peace time on a sound and profitable basis becomes one of the most economic and sensible schemes for the national defense.

SURGERY

Alcohol is a necessary chemical in the maintenance of our hospitals. Modern surgery would not have been developed if it were not for anesthetic ether. This ethyl ether is a dehydration product of alcohol and has never been completely satisfactory, so many other anesthetics, such as nitrous oxide and chloroform, have been tried. Recently ethylene, another dehydration product of alcohol, has attracted the attention of the surgeons throughout the world. This gas has a rather pleasant, sweet odor and seems to produce anesthesia more easily and with less bad after-effects than any other anesthetic. It will not only render the patient unconscious, but it can be so used that the patient will be devoid of pain while understanding everything that is going on about him and with a certain amount of control over his body. It is hoped that ethylene will prove satisfactory as a pain reducer for use in obstetrics. Should such be the case, it will be one of the greatest medical discoveries of all times. Chloral, chloroform, iodoform, and ethyl chloride are all used in hospitals extensively and all are made from alcohol. Alcohol itself is used both for sterilization and as an antiseptic.

DYES

The American dye industry, which everyone now realizes is an important factor in national defense be-

cause every dye plant is a potential high explosive plant, depends upon alcohol as one of its chief raw materials. Alcohol is used in many different ways in the manufacture of dyes. Each dye is a complicated chemical problem and involves the use of many different chemical compounds but especially alcohol.

ARTIFICIAL SILK

Artificial silk is fast becoming a huge industry in this country and requires large quantities of alcohol. This artificial textile has qualities not possessed by real silk. The gloss, or high luster, is far superior to that of natural silk. Artificial silk, depending upon the type and quality, absorbs dyes in a manner different from real silk. Many of the beautiful gowns seen in the exclusive shops along Fifth Avenue and Fifty-seventh Street, New York, are made with artificial silk.

If it were not for the large production of artificial silk the price of hose made from natural silk would be beyond the reach of the average purse. Finer types of this textile may be expensive but the beautiful color and texture are unsurpassed. The present yearly production is seventy million pounds.

PRINTING AND PHOTOGRAPHY

The printing, engraving, and photographic industries all use alcohol. The modern engraver uses alcohol in the dyes and in the coatings for his paper and his cuts when he makes his beautiful colored prints. Photography, especially in the moving picture industry, uses millions of miles of nitrocellulose film per year. This film requires alcohol in its production.

Even the solutions which are deposited upon the film and the solutions which are placed upon paper in order to bring out the image produced by the effect of light, require alcohol in their manufacture.

The tanning industry, the linoleum industry, the casein industry, all use large quantities of alcohol; even plants that manufacture fireworks cannot get along without alcohol.

Millions of odds and ends such as ships' compasses, levels on surveying instruments, thermometers, solder fluxes, and etching solutions, all require alcohol in their manufacture. Perhaps the most important miscellaneous use is alcohol for scientific purposes. The advancement of civilization, the constant increase of comfort to the individual, and the increase of the capacity for appreciation of life, or, in other words, the accumulation of knowledge is perhaps the most essential thing to foster. Alcohol aids materially in this great work.

It is impossible for the human race to do without alcohol. They are washed with it at birth and embalmed with it after they are dead, and use it constantly in the meantime.

Absolute Ethyl Alcohol

Within the last two years a new commercial product has been manufactured and placed on the market in large quantities. This is an anhydrous ethyl alcohol. The ordinary alcohol is 95 per cent alcohol and 5 per cent water. Ordinary distillation methods will not remove this 5 per cent of water because it is the nature of ethyl alcohol to hang on tightly to this amount of water. A few years ago anhydrous or absolute alcohol sold for from ten to twenty dollars a gallon. It now

sells for less than one dollar a gallon. Previously it was a chemical rarity sold in small glass bottles. It is now sold for plant use in tank cars (8000 gallons capacity).

This absolute alcohol has entirely different physical properties from the old 95 per cent product. It will dissolve many things that the other would not. Chemists can make use of this new commercial product in ways which will mean immense savings in other industries. It is this product that is used with gasoline to make motor fuels.

Methyl Alcohol

Methyl alcohol, or wood alcohol, is made by the distillation of wood during the production of charcoal. It is one of the volatile constituents that comes over in the distillation. Organic acids, such as acetic, also come over; these are neutralized and the remaining crude methyl alcohol distilled off. This crude liquor is refined by another distillation.

Methyl alcohol has been used for a great many years in the dye industry and as a solvent in many industries. It is the raw material from which all formaldehyde, the well-known disinfectant, is made. Because of its poisonous properties, in recent years it has been replaced somewhat as a solvent by ethyl alcohol. This fault is turned into a virtue when methyl alcohol is used as a denaturant for ethyl alcohol.

Methyl alcohol production is very limited because as yet it is only obtained as a by-product of hardwood distillation. Our forests are rapidly becoming depleted and the production of methyl alcohol is obviously essential, so many attempts have been made to obtain this product from some other more abundant source. These

attempts so far are failures, but when the demand is great enough the new process will be forthcoming. This is another excellent opportunity for some chemist to acquire fame and possibly fortune.

In the refining of methyl alcohol three interesting by-products are produced. One is a mixture of methyl alcohol, acetone, and methyl acetate, called methyl acetone, and is used in large quantities as a paint remover. Another is a mixture of ketones which is used as a solvent in the lacquers for airplane wings. Still another is allyl alcohol, a peculiarly irritating liquid which is made into a compound forming the basis of an ointment which is used for colds, sore throat, etc. This compound made from allyl alcohol is a synthetic mustard oil.

Other Alcohols

Isopropyl alcohol is made in small quantities from the vapors coming off of stills that are used to break down oil to form gasoline. It resembles ethyl alcohol and because of its high price has very little use except as a denaturant for ethyl alcohol. Though this product seems to have no important individual uses, nevertheless a process to make it at a cost near that of ethyl alcohol would be appreciated, and the inventor would be rewarded.

Butyl alcohol (normal) is made by the action of certain bacteria on corn. The process resembles ordinary alcohol fermentation but is not so easily operated. This alcohol has been found to be a successful substitute in many cases for amyl alcohol, and is used in large quantities as a high-boiling solvent for nitrocellulose and gums. Attempts have been made to make this alcohol synthetically from acetylene gas and from ethyl alcohol, but these processes are not in operation

on a commercial scale. A cheap and smooth-running synthesis of butyl alcohol would be appreciated by the manufacturer of pyroxalin plastics, films, and lacquers.

The field or high-boiling alcohols have not been thoroughly covered and there is room for improvement. It is hoped that some chemist will develop a cheaper and better alcohol of this type because of its importance and use as a solvent.

Ethyl Acetate

Ethyl acetate is an ester, the product of an alcohol and acetic acid. Water is also formed. The reaction may be written:

Ethyl Alcohol		Acetic Acid		Ethyl Acetate		Water
C_2H_5OH	+	CH_2COOH	=	$CH_3COOC_2H_5$	+	H_2O

This solvent is extremely useful, especially in the manufacture of artificial leather. Most of our automobiles use this substitute for leather for seat and top coverings. Chairs are upholstered with it. Ethyl acetate can be dehydrated in a manner similar to the dehydration of 95 per cent ethyl alcohol. The resulting anhydrous product has been found to be useful in the manufacture of nitrocellulose films and lacquers. It is a valuable constituent in paint removers. Still other uses could be found for the new commercial solvent and large savings would be realized.

Other Esters

Amyl acetate, made from amyl alcohol and acetic acid, has been used for many years in the pyroxalin industry. The limited supply of amyl alcohol has prevented its development.

Butyl acetate resembles amyl acetate and is used in certain cases as a substitute for the latter.

Ethyl acetoacetate is made by the action of metallic sodium on anhydrous ethyl acetate. It is the base for the manufacture of antipyrin and certain yellow dyes. It has never been used extensively as a solvent owing to its high cost, but it is a solvent with exceptional properties.

Ethyl lactate, made from ethyl alcohol and lactic acid (this acid is sour milk), has been used as a solvent for cellulose acetate in the manufacture of noninflammable "dope" for the airplane wings used by the United States Army. Germany is also a large user of this solvent. So excellent a solvent should have more uses.

Ethyl oxalate, made from ethyl alcohol and oxalic acid (the acid used for cleaning hats), is used in synthetic work but should prove to be a desirable high-boiling solvent.

Methyl acetate, recovered from wood distillation and also made from methyl alcohol and acetic acid, had a large war-time use in airplane lacquers. The production is limited because of the small production of methyl alcohol.

Diethyl phthalate, a practically odorless high-boiling ester, is made from ethyl alcohol and phthalic anhydride (made from coal tar). This is an excellent solvent for pyroxalin and because of its freedom from odor should prove to be popular.

Cresyl phosphate is used because of its extremely high boiling point in the manufacture of films. It reduces the flammability of the resulting product.

The list is almost limitless, and yet the ideal ester with a high boiling point has not appeared on the market. It must be cheap, odorless, unlimited in sup-

ply, and it must act as a solvent for many different substances. The requirements are rigorous but it will be produced.

Ethyl Ether

Ethyl ether or ether is the well-known anesthetic. It is made by the dehydration of alcohol. The reaction may be written:

Ethyl Alcohol		Ethyl Ether		Water
$2C_2H_5OH$	=	$(C_2H_5)_2O$	+	H_2O

It has been used for a long time with alcohol as a solvent for collodion. At present it is extensively employed as a solvent in the manufacture of artificial silk. It is also used in large quantities to extract volatile oils from plants. Where a highly volatile inert solvent is needed, ethyl ether answers the purpose.

The other ethers are chemical rarities because the corresponding alcohols from which they are made are too costly.

Acetone

Acetone is a ketone and is recovered in wood distillation. It is also made by heating calcium acetate as follows:

Calcium Acetate		Acetone		Calcium Oxide		Carbon Dioxide
$CH_3COO\diagdown$ $\quad\quad Ca$ $CH_3COO\diagup$	=	$CH_3\diagdown$ $\quad\quad CO$ $CH_3\diagup$	+	CaO	+	CO_2

Recently it has been made as one of the products in the butyl alcohol fermentation of corn. During the World War, the entire production of acetone was used as a solvent for cordite, the British high explosive.

In peace time it is used in paint removers and as a solvent for acetylene. The use of this product should be developed as a means of national defense. Some work has already been done in this direction.

One other ketone has been mentioned under methyl alcohol by-products. The rest are not important at this time, principally because of the scarcity of raw material for their manufacture.

Benzene

Benzene is a hydrocarbon recovered from coal by distillation. It is not a very active solvent but acts as an excellent diluent when used with an active solvent. It has been used successfully as a motor fuel in conjunction with gasoline, but the supply is limited and it can never be a factor in this field. It is the basis for many dyes, but our dye industry requires only a small percentage of the total supply. It is in the solvent field that benzene will be used to best advantage.

Other Hydrocarbons

Toluene is the well-known base for TNT and comes from coal tar. It resembles benzene in solvent powers.

Gasoline is a good solvent for some substances and its use in dry cleaning is familiar to everyone.

Hexane, or petroleum ether, is a volatile constituent of gasoline and has particular solvent powers. It is used for extracting oils somewhat similar to ethyl ether.

Chlorinated Hydrocarbons

Hydrocarbons which have one or more of their hydrogen atoms replaced by chloride are called chlo-

rinated hydrocarbons. Carbon tetrachloride (CCl_4) is the chief constituent of small fire extinguishers. It is noninflammable and quite inert. It, therefore, makes an excellent solvent in industries where there is a fire hazard.

Chloroform ($CHCl_3$) is the well-known anesthetic. It so happens that it is also an excellent solvent for cellulose acetate. The latter is used in noninflammable films. The cost of manufacture of chloroform has prevented its extensive use.

Conclusions

New processes of manufacture and new uses for alcohols and solvents offer a field in which the research worker can find plenty of opportunity and ample reward for his inventive genius.

CHAPTER IV

COAL, COKE, AND THEIR PRODUCTS

F. W. Sperr, Jr.
Chief Chemist, The Koppers Company

"The future belongs to the nation which makes the best use of its coal resources." This statement, made in 1910 by a German writer, is now even more true than the words uttered one hundred years ago by the great English financier and statesman, Sir Robert Peel, who said that the future belonged to the nation which could produce the most coal.

Bearing in mind that coal or material produced from coal is used for practically all domestic and industrial heating, and as the principal source of power for railroads and steamships, that coal or material produced from coal is indispensable in the manufacture of iron and steel, and that thousands of useful by-products are derived from coal, it can be realized that a sudden stoppage of coal supply would be an unbearable blow to civilization.

It is a fact that modern civilization is founded on coal and iron. Coal and iron are linked by coke, and in making coke other materials called by-products are produced, from which modern chemistry has developed thousands of new products indispensable to present-day standards of living. From the by-products of coke manufacture are derived fertilizers, explosives, food

preservatives, disinfectants, antiseptics, perfumes, photographic materials, roofing compounds, road material, wood preservatives, medicines such as aspirin, acetanilide and many others, flavoring compounds such as vanillin, and practically all of the dyes used in the modern textile industry. Modern engineering has developed the by-product coke oven which makes it possible to save these by-products, formerly thrown away as of no importance. And these by-products and the materials derived from them are even more vital in war than in peace.

The Formation of Coal

Let us begin with fundamentals and find out first what coal really is. Every step in the formation of coal is a wonderful example of chemical processes occurring on a gigantic scale in the laboratory of Nature. There is a remarkable cycle in the formation of coal, in its combustion, and in the possibility of forming coal again from the products of combustion. Coal is formed from peat, and peat is formed from plants. The principal component of all these is carbon, which is the fundamental chemical element in every living substance. Now, strange to say, the carbon which goes to build up plants is essentially derived from the atmosphere, in which it ordinarily occurs in so small a quantity that one seldom thinks of it as being an essential constituent. Ten thousand volumes of air contain about three volumes of carbon dioxide (CO_2). In other words, the air in a room 15 feet wide, 20 feet long, and 11 feet high contains about 1 cubic foot or a little less than two ounces of carbon dioxide. Of this, less than one ounce is carbon. Nevertheless it is this carbon which nourishes plant life. From plant sub-

stance, first peat and then coal are derived through long periods of time. Coal is burned, producing carbon dioxide, and thus we may conceive that the cycle is perpetually renewed.

But coal itself will not grow like a plant. Definite conditions are required for its production. Geologists tell us that the conditions most favorable for its formation are found in fresh-water lakes bordered by flat, marshy land, on which an abundance of vegetation grows. The vegetation grows, decays, and grows again, pushing its way out into the lake and gradually building up on the bottom a mass of peat which becomes thicker and thicker as the years progress. The process may be aided by gradual subsidence of the land. The Dismal Swamp of North Carolina and Virginia is a good example of such a process occurring under our own eyes. Eventually, under the influences of slow decay and pressure, the peat is hardened into a material called lignite. Recently formed lignite has a brown color like that of the original peat, but the older varieties of lignite are black, very much like ordinary coal.

As hundreds and thousands of years pass on, the layers of peat or lignite are covered deeper and deeper by masses of clay and sand which harden into rock. The material may become heated through chemical agencies or even by actual volcanic heat. The agencies of heat and pressure and chemical action combine to produce ordinary coal, and in long ages this may become hard coal or anthracite. Estimates as to the amount of time required to produce coal vary greatly. One estimate is that 1 foot of peat is formed every hundred years, and that 3 feet of peat are required to make 1 foot of coal. It is also stated that about

20 feet of the original decayed plant substance are required to make one foot of coal. Most of the great coal seams which are now being mined are believed to have been formed forty million to one hundred and fifty million years ago, so that the actual time of their formation was very short as compared with the long aging that they have subsequently undergone. It is an interesting fact that it is possible to make artificially a material very much like coal by subjecting vegetable matter to heat and high pressure.

Considering the complicated nature of the materials from which coal is formed and the enormous spaces of time during which the various natural agencies have exerted their action, it is not surprising that coal is a very complicated substance, and that different coals may be quite different in their properties. The surprising thing is that they are so much alike. The actual chemical nature of coal is very little understood. The chemist can say that coal is composed essentially of carbon, hydrogen, and oxygen, with a little nitrogen and a little sulfur, and more or less mineral matter which is responsible for coal ashes. Ordinary bituminous coal, after drying, has about the following composition:

	Per cent
Carbon	75.0
Hydrogen	5.0
Oxygen	7.0
Nitrogen	1.4
Sulfur	1.6
Ash	10.0

This, however, does not tell the real nature of the chemical compounds in coal, and many chemists are

now at work endeavoring to disentangle and identify these compounds.

So much space has been given to discussing the formation of coal because the chemist believes that with a thorough knowledge of this he will be better able to understand the behavior of coal and the character and quality of the products derived from it.

In the mining of coal the chemist is principally concerned with analyses which enable him to determine the quality of the coal which is being mined, its freedom from impurities, and the best commercial use to which it can be put. Space forbids a detailed discussion of mining, since we are principally concerned with the question of utilization.

The Utilization of Coal

By far the greatest amount of the coal which is mined is burned directly without any treatment. The amount so burned in the United States is measured by millions of tons. About two hundred and fifty million tons are burned for various industrial purposes, and more than sixty million tons are consumed in domestic heating. Here is one of the most important and attractive fields for the chemist. Every ton of coal burned directly means a large waste of valuable material.

In the first place, there is a waste because such burning is seldom done efficiently. In many cases perhaps one-fourth of the heating value of the coal may be utilized, while the other three-fourths is absolutely wasted. Thus, a large part of the labor of mining the coal and of the effort and expense of transporting it, as well as the intrinsic value of the coal itself, are lost. The smoke nuisance must also be considered. The actual amount of carbon in smoke may be compara-

tively small, but the damage to property and the increased cost of cleaning and laundering which result from it amount to millions of dollars annually, while the injury to health cannot be estimated in dollars.

In connection with the direct burning of coal there is, therefore, a great deal of research along the lines of accomplishing the burning more efficiently. Some improvement can be effected by properly designed mechanical stokers, and much can be done by chemical control of the combustion process. Automatic apparatus has been invented for continuously analyzing the products of combustion and recording the analyses on charts operated by clockwork in view of the fireman who can regulate his operation accordingly.

A second line of development in direct burning consists in pulverizing the coal very finely. The fine coal dust, fed through a burner and ignited, burns very much like a gas and in properly designed apparatus the combustion can be accomplished very efficiently.

The Production of Gas

It is easier to control the burning of a gas than that of a solid material and important developments have been made in connection with completely gasifying the coal before burning it. The apparatus used is called the gas producer, and the resulting gas is called producer gas. The principle of the gas producer is an excellent example of the application of studies of very simple chemical reactions to a great industry. Gas producers depend upon the fact that there are two gaseous compounds of carbon and oxygen—combustible carbon monoxide and incombustible carbon dioxide. When carbon is burned with a small amount of oxygen, conditions may be controlled so that the com-

bustible carbon monoxide is the principal product. When air is used to supply the oxygen, the reaction is:

$$2C + O_2 + (\text{nitrogen}) = 2CO + (\text{nitrogen})$$

The products of the reaction—carbon monoxide and nitrogen—constitute the producer gas. If this producer gas is used hot, the total efficiency, based on the original carbon, may be from 85 to 90 per cent, the reaction being:

$$2CO + O_2 + (\text{nitrogen}) = 2CO_2 + (\text{nitrogen})$$

The mixture of carbon monoxide and nitrogen, produced as indicated above, is often called air gas. In ordinary producer practice, some steam is admitted with the air. This affords means of preventing excessively high temperatures and produces a richer gas containing hydrogen in addition to the carbon monoxide, the principal reaction being:

$$C + H_2O = CO + H_2$$

This is the water gas reaction which is utilized in another process, the manufacture of water gas. Although bituminous coal is sometimes used for the manufacture of water gas, the materials most widely employed are coke or anthracite. The water gas may be either blue gas (so called from its characteristic blue flame) or carbureted water gas. In the manufacture of blue gas, the fuel is placed in a cylindrical container called the generator. The bed of fuel is first brought to a high temperature by blowing air into the generator, the products of combustion passing through a waste heat boiler to recover their heat and then into the atmosphere. When the desired temperature is reached, the air is turned off and steam is blown

into the generator, producing water gas according to the above reaction, this gas being conducted to the holder or point of utilization. After a short period of steaming the temperature falls to a point where the reaction can no longer be efficiently maintained. The steam is then cut off and the air turned on again. The operations of blowing and steaming are thus carried on alternately, fresh fuel being added to the generator from time to time.

For the manufacture of carbureted water gas, two additional vessels filled with checker work are placed between the generator and the waste heat boiler. These are called the carbureter and superheater. The operations are carried on as in the manufacture of blue gas, the products of combustion passing through the carbureter and superheater and heating these to a high temperature. When steam is admitted to the generator, oil is sprayed into the carbureter where it produces a rich gas which is rendered more stable by passing through the superheater. This oil, mixed with the blue gas, produces a gas of higher heating value, the heating value being controlled by the amount of oil used. The manufacture of carbureted water gas is of great importance, supplying more than half of the artificial gas consumed for domestic purposes in the United States.

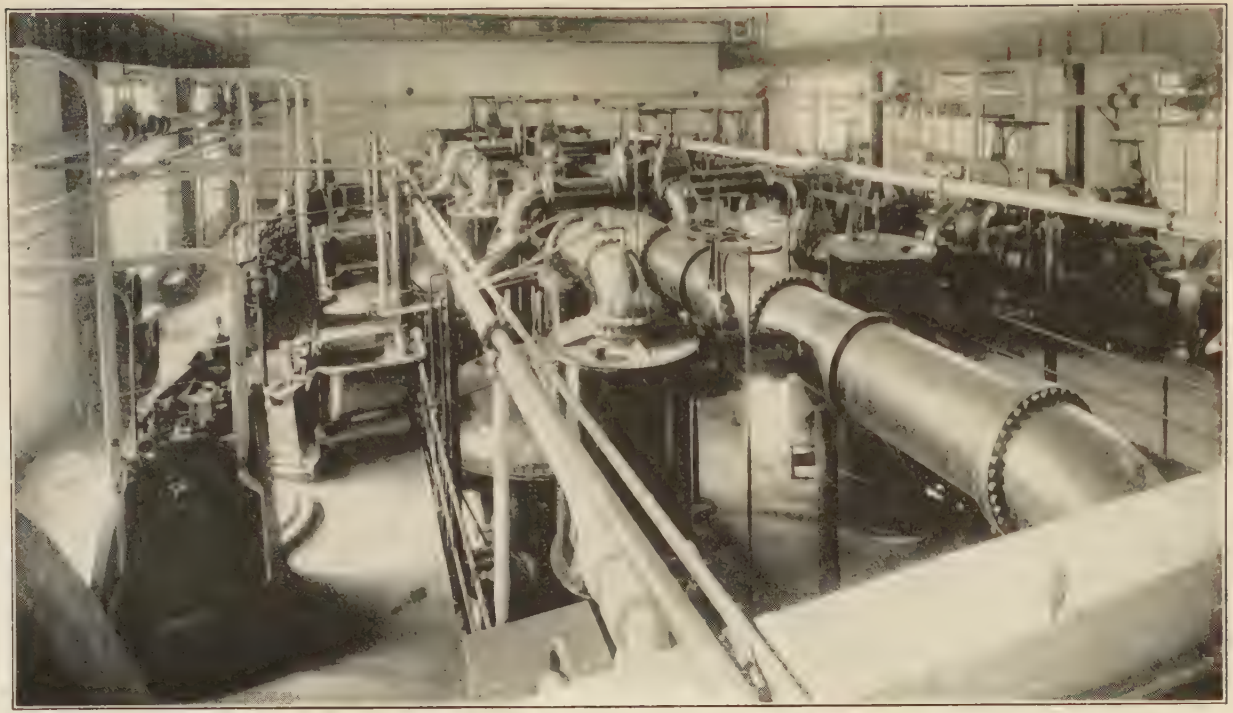
By-Product Recovery

We have now briefly considered the utilization of coal by direct burning or by complete gasification and burning without recovery of the by-products which are of such inestimable value in all walks of life. There are types of gas producers, known as by-product recovery producers, which make possible the recovery of

tar and ammonia in connection with the complete gasification of coal. There are several of these plants in Europe, but they have been introduced to only a limited extent in America. There is a growing feeling that coal should first be treated for the recovery of by-products and that the residue from such treatment should be burned instead of the raw coal.

It required such an emergency as the World War really to emphasize this fact to the American people. Important as coal and its by-products are in peace times, they are still more important in war, and the strategic importance of coke oven by-products and the materials derived from them through the application of chemistry come into startling prominence.

The best high explosives, such as trinitrotoluene (the famous TNT) used by modern artillery, are derived from the by-product coke oven. It has often been stated that the striking power of a nation is in proportion to its supply of the by-products of coke. It may not be realized that some of the principal elements of strategy in the World War had to do with the manufacture of by-product coke, and a great deal of the political strategy since the war has had to do with this same matter. At the beginning of the war Germany was well prepared with by-product coke ovens, as with most other things, while the Allies were sadly unprepared. All the coke used in Germany was made in by-product coke ovens, while much of that used in the other countries was made in beehive ovens in which the by-products were entirely wasted. Germany was then producing more of the by-products of coke than all of the Allies combined. She was producing four times as much of these products as the United States, in spite of the fact that the United States was producing much more coal.



Courtesy, The Koppers Company.

Interior of By-Product Recovery Building.

The first act of Germany was to seize Belgium, Luxembourg, and northern France, largely because the principal by-product coke industry of the continent of Europe outside of Germany itself lay in these regions. This seizure gave Germany far more by-product coke-oven resources than all of the rest of the world combined. The success of this seizure, as exemplified by the rapid destruction and capture of such impregnable fortresses as Namur, Maubeuge, and Antwerp, was due very largely to the marvelous high explosives developed by German chemists and originating in German by-product coke ovens.

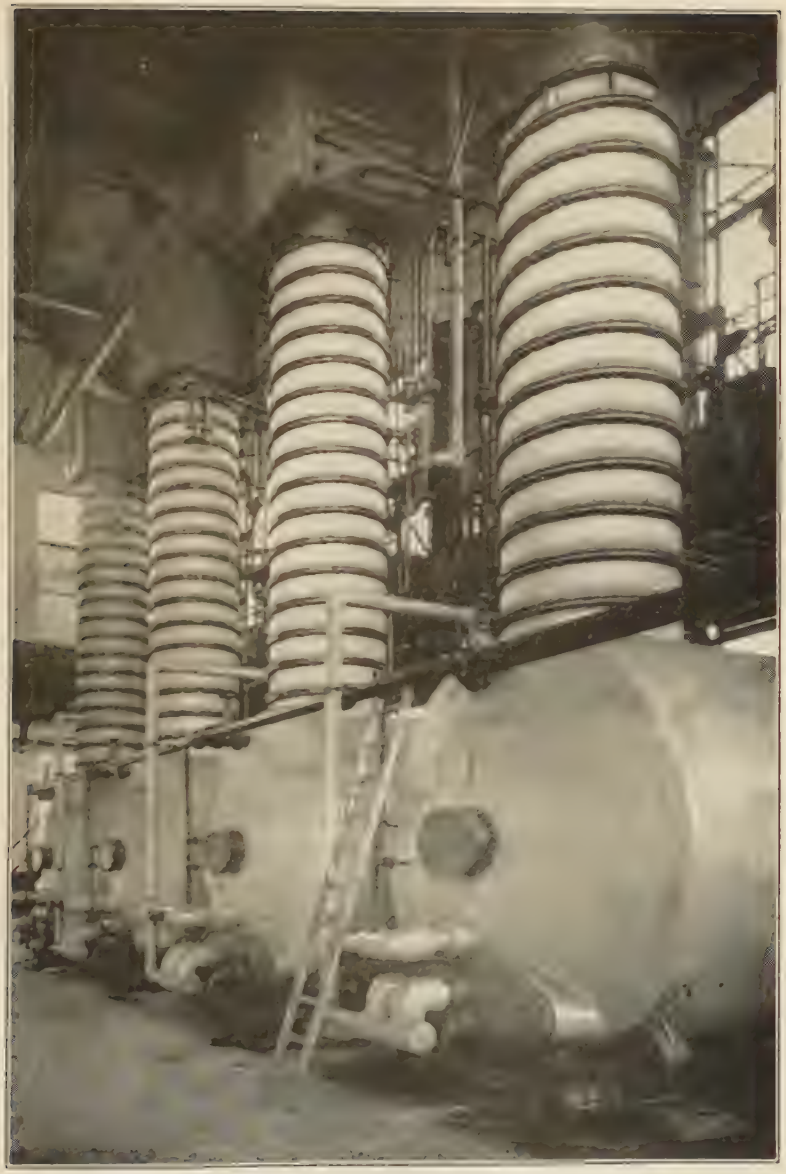
For a long time the Allies were engaged in feverish efforts to overcome their tremendous handicap in by-product coke oven resources. In America the construction of by-product coke ovens was pushed by private manufacturers with all possible energy, and when this country entered the war the Government itself lent aid in the construction of new ovens. The resulting improvement in the conservation of our natural resources is one of the few permanent benefits resulting from the war, and it is to be hoped that the lesson of the importance of such resources in national defense will never be forgotten. The United States is now producing more of the by-products of coke than any other country, but 30 per cent of its total coke production is still made in the wasteful beehive ovens, and far more is wasted by direct burning without recovery of the by-products.

In order to understand the possibilities in this connection, we must consider what happens when coal is heated in a closed chamber or vessel out of contact with air. Leaving out of account anthracite, which does not produce any value in the way of by-products and which is a proper fuel for direct burning, we may divide the

various coals roughly into three groups—coking coals, poorly coking coals, and noncoking coals. Geologically, the greater the age of a coal the better are its coking qualities. Lignite or "young coal" is noncoking. Chemically, the higher the percentage of oxygen in a coal the poorer is its coking quality. Most of the bituminous coal now mined east of the Mississippi River and a considerable portion of that mined west of the Mississippi is coking coal.

When a coking coal is heated in a closed chamber, it first softens at about 350° Centigrade, then, as the temperature increases, gives off tarry vapors and gases, the residue hardening to a bright, gray mass called coke. Good coke forms fairly large, firm pieces filled with cells resembling those of a loaf of bread. In the case of poorly coking coal, the pieces of coke are slender and brittle, the cells are irregular, and much of the material may not produce coke at all. When noncoking coals are heated, the fragments of the original coal do not soften and do not change their shape. A considerable amount of gas and tarry matter is evolved, but the residue has much the appearance of the original coal.

The by-products, from which such valuable products are obtained, are all contained in the gases and vapors evolved during the heating of coal out of contact with air. Gas is itself a by-product. Although there are a multitude of substances in these gases and vapors, the ordinary by-product coke plant or gas works produces only four primary products—gas, tar, ammonia, and light oils (benzenes), which are sold to consumers or to manufacturers of other products. Sometimes cyanogen compounds and sulfur are recovered as by-products; while in gas-works practice, the light oils or benzenes are not usually recovered. It is



Courtesy, The Koppers Company.

Distillation Apparatus for Production of Benzene, Toluene, Solvent Naphtha and Motor Fuel.

probably not too much to say that some of the most important developments in modern chemistry have been due to studies of the substances found in these products. No other field has attracted so vast an amount of research, and no other field has yielded richer returns. Yet there are still many substances which have not been studied and many for which no commercial use has been found.

High Temperature Carbonization of Coal

The heating of coal out of contact with air is called carbonization. Practically all the recovery of by-products now carried on is done by high temperature carbonization, by which we mean that the coal is heated to a temperature of approximately 1000° Centigrade. There are two sorts of high-temperature carbonization processes—one employing the gas retort and the other the coke oven.

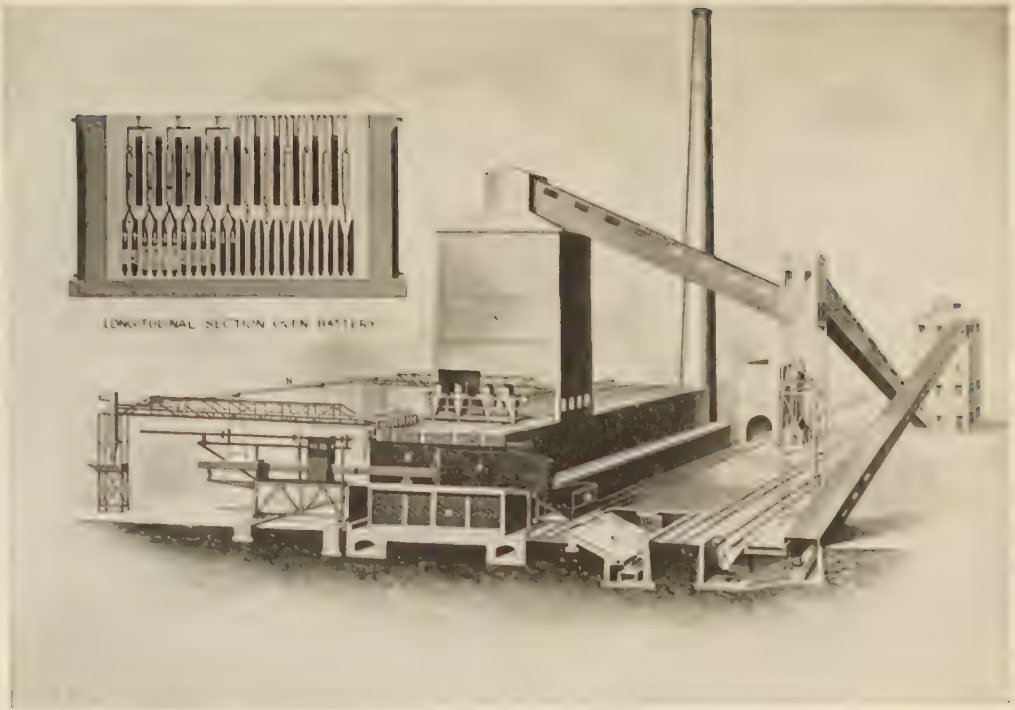
The gas retort is in principle a long and comparatively narrow tube, while the coke oven is a long, high, narrow chamber. The gas retort, as its name indicates, was developed primarily for the purpose of making gas, and produces a comparatively poor coke.

The modern by-product coke oven has been so improved that it can be counted on to make both good gas and good coke, and the gas industry is rapidly substituting it for the retort. Considerably more domestic coal gas is now made in coke ovens than in retorts.

The by-product coke industry is a comparatively new one, having its commercial beginning only about forty years ago. It was first developed to furnish coke for the manufacture of iron. Most of the coke previously made was manufactured in beehive ovens in

which all of the by-products were wasted. This waste was realized and a great deal of work was done in the invention of means for coking coal in closed chambers arranged so that the by-products could be recovered. There were many engineering difficulties and problems to be overcome and for many years the by-product coke oven underwent very slow development. Great impetus was given to the industry by the inventions of Heinrich Koppers, who succeeded in overcoming most of the major difficulties and whose ovens were introduced into the United States by the United States Steel Corporation in 1910. Most of the by-product coke ovens now in operation in the United States have been built by The Koppers Company of Pittsburgh. A few years ago Joseph Becker of this company invented what is now known as the Becker oven, and all of the ovens built during the past two years are of this type.

The picture shows the essential arrangement of a modern by-product coke plant. The coal is discharged from railroad cars into the hoppers, *A*, and from these it goes on belt conveyors to the top of the breaker building, *B*, where it is broken up to about 1½-inch size and under. Any hard refuse material is removed here. Many plants employ pulverizing apparatus in addition to the breakers, pulverizing the coal to about ⅛-inch size. This is especially necessary where two or more coals are mixed for the sake of regulating coke quality. From the bottom of the breaker building the coal is transferred to the large bin, *C*, which has sufficient capacity for twenty-four hours' operation. Each charge of coal for the ovens is taken from the bin, *C*, by the larry car, *D*, which has four cone-shaped hoppers corresponding with four holes on the top of each oven.



Courtesy, The Koppers Company.

Arrangement of Modern By-Product Coke Plant.

During the coking period the gases pass from the ovens into the collecting main, which is sprayed with tar and ammonia liquor so as to effect preliminary cooling of these gases. The gases then go through the pipes, *N*, to coolers and then to the by-product building. Here the last traces of tar are removed and ammonia is recovered, usually by means of sulfuric acid, making the important fertilizer ammonium sulfate. In a separate system of apparatus, the benzenes, important for the numerous valuable chemical compounds derived from them, are recovered.

The coking period in modern operation is about twelve hours. The great progress made in the development of this industry is shown by the fact that a single oven of the Becker type cokes its charge in twelve hours and has a capacity of thirty tons of coal per day, while the ovens of a few years ago had a coking time of about sixteen to eighteen hours and a capacity of eighteen to twenty tons of coal per day.

When the coking is completed, the oven doors are removed and the coke is pushed out by means of an electric ram known as the pusher. The red hot coke falls into a quenching car, *H*, which is transferred by an electric engine to the quenching tower, *J*. Here it is cooled with a shower of water. The quenching car is then moved to the wharf, *K*. Coke is discharged onto this wharf and thence goes through a system of belt conveyors to the screening station where it is assorted into the various commercial sizes.

The by-product coke ovens are arranged side by side in batteries of from five to one hundred ovens. Each oven is a long, narrow chamber built of silica brick, having an average width of fourteen inches, a height of twelve feet, and a length of forty feet. Between each two ovens is a series of vertical flues in which

gas is burned to supply the necessary heat. It is most important that the temperature of the walls be uniform, and the uniform heating of thousands of square feet of brick surface to a bright yellow heat is one of the marvelous accomplishments of modern engineering. Beneath the ovens are the regenerators which conserve the heat in the burnt gases and utilize it for preheating the air used for combustion.

The following products are obtained from one ton of Pittsburgh coal:

Total coke	1500 pounds
Gas	11,360 cubic feet
Tar	12.4 gallons
Ammonium sulfate.....	25 pounds
Light oil (benzenes)....	4 gallons

In the beehive oven, everything except the coke is wasted and moreover a smaller yield of coke is obtained. When it is realized that about forty million tons of coal are coked per year in by-product ovens, the enormous saving already accomplished can be appreciated; but several million tons of coal are still being coked in beehive ovens, and two hundred and fifty million tons of coal are burned each year without the recovery of by-products. We have scarcely approached the possibilities of saving these valuable resources.

Low-Temperature Carbonization

In recent years much study has been made of low-temperature carbonization, in which coal is heated to approximately 500° Centigrade. The products obtained in this case are quite different from those obtained in high-temperature carbonization. The yield

Courtesy, The Koppers Company.

Ammonium Sulfate Storage.

of tar is greater, it is thin and oily, and varies greatly in composition from ordinary coal tar. The yields of gas and ammonia are much less than those obtained from the by-product coke oven. The gas has a higher heating value and is different in composition. The light oils also are radically different. The residue, unlike coke, is black, soft, and spongy, but like coke burns with a smokeless flame. Many attempts have been made to conduct low-temperature carbonization on a commercial scale, but there are many engineering difficulties to be overcome and no attempt can yet be considered successful. Low-temperature carbonization produces a large number of compounds which are very interesting to the chemist because of their novelty, but so far no important commercial use has been found for any of them in the chemical industries.

There is no field in industry which offers greater possibilities for scientific research than the utilization of coal, and the greatest hope for improvement in the utilization of the coal resources of any nation lies in the developments of chemistry. While most by-product recovery is through high-temperature carbonization, low-temperature carbonization, which has just been mentioned, may be compared to a new and unexplored continent of which we scarcely know the shore line. With coal, in the very first place, we are dealing with a material of which we do not even know the primary composition. Each new product derived from coal opens a new field of research in itself. North America has been more richly endowed with coal than any other continent and most of this is in the United States. As a nation, we produce far more coal than any other, and so we measure up to Sir Robert Peel's standard of a century ago. But this is not enough.

It is not the nation which produces the most coal, but the one that makes the best use of its coal resources that will survive.

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CHAPTER V

COTTON AND COTTON PRODUCTS

THOMAS C. LAW

President, Law & Co., Inc., Consulting and Analytical Chemists

Probably the greatest question in regard to the recent World War is "Who won the war?" There have been numerous answers to this question, and yet it will never be answered to the satisfaction of all. If I were asked "*What* won the war?" I would unhesitatingly answer, "The cotton plant." Let us consider for a moment some of the things the cotton plant contributed. The four outstanding things required by a soldier in any war are food, clothing, housing, and ammunition.

Second only in importance to the nitrogenous foods for soldiers are the fats that they must have. Most of the lard consumed by our armies was compound lard, made from cottonseed oil. Much of the butter they ate was oleomargarine, of which cottonseed oil was the principal component. The dairy products and meat which they consumed came from cattle largely fed with cottonseed meal and hulls.

Much of the clothing of our soldiers was made of cotton. Their hats were made of felt, a product of cotton linters. The buttons on their uniforms, when not metal, were of celluloid, also a product of cotton linters. The artificial leather used in their equipment

was made from cotton linters, and the real leather came from cattle which were fed on cottonseed meal and hulls.

The tents which covered our soldiers were made of cotton; the mattresses upon which they slept were stuffed with cotton linters and their bedclothes were either made from cotton or from wool of sheep which were fed to a large extent on cottonseed meal.

The basis of ammunition, or explosives, was cellulose and glycerides, one coming from cotton linters and the other from cotton oil. This was such an important factor during the World War that the War Department took over all the cottonseed oil mills and operated them under license.

Can you find one single source that contributed so much to the welfare of our soldiers as the cotton plant? It may not have won the war, but we certainly could not have won without it.

In this chapter we are not to discuss textile chemistry, other than to mention the fact that chemistry is today playing a most important part in the cotton mill.

Special reference to the cotton fiber will therefore be omitted and we will deal rather with the less familiar composition and chemistry of the cottonseed. Have you ever seen a cottonseed? It is a little insignificant object of oblong shape about the size of a B B shot and made up of three component parts, viz., a fuzzy lint which is left when separating the fiber from the seed in the gin, a thin, woody hull, and a yellow, meaty kernel. This kernel is subdivided into two parts. If we examine it carefully we will see minute brown specks. Under a microscope these are shown as oil cells. They contain the oil of the kernel which is about

one-third of its weight. So the two products of the kernel are the meal and the oil.

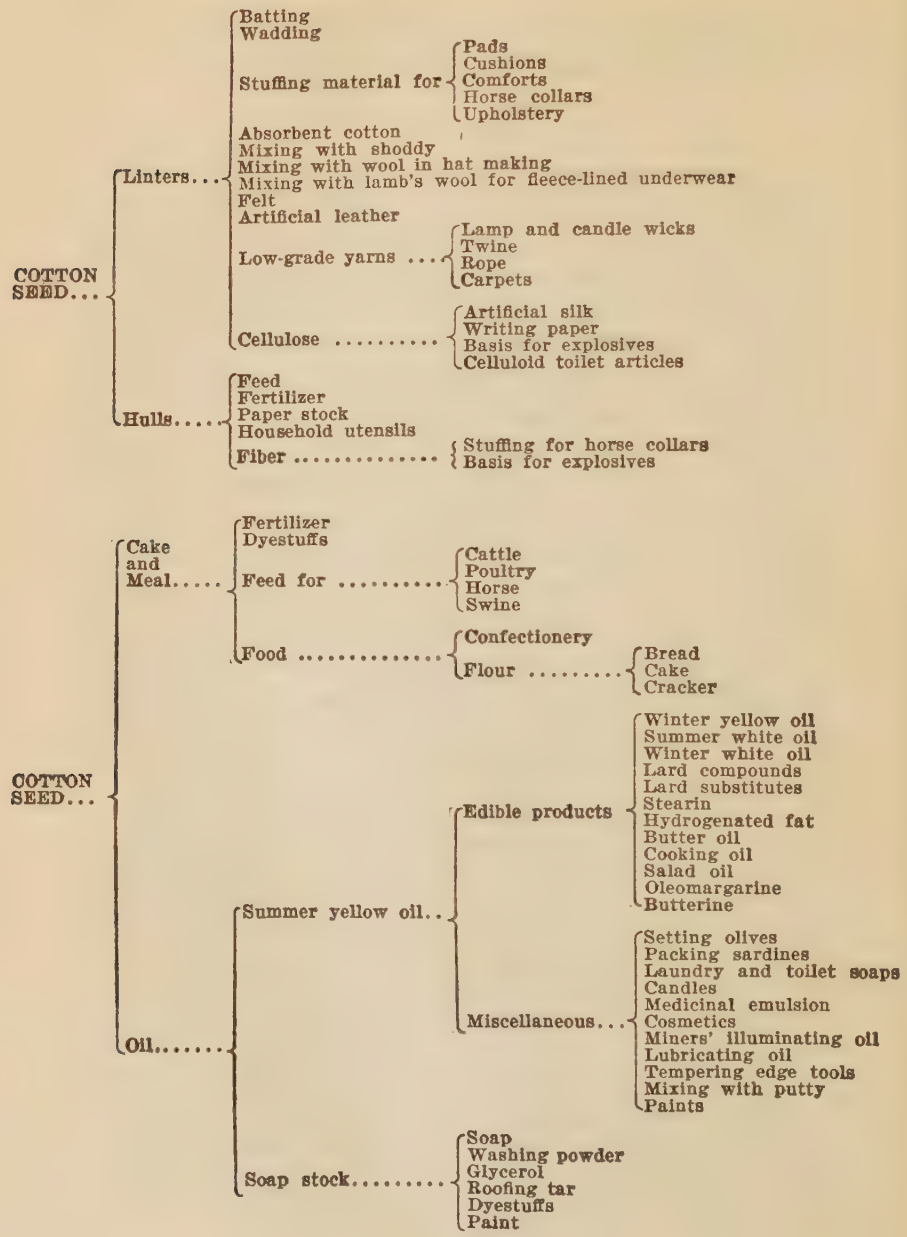
Cottonseed Products

Thus the cottonseed produces four main products: the linters, meal, hulls, and oil. A résumé of the history of the cottonseed products industry will show that within a space of half a century the chemist has developed from this little insignificant seed sixteen principal commercial products and hundreds of minor ones.

Fifty years ago the problem at many gins was what to do with the cottonseed. In some sections of the Southeast they were used as a fertilizer, or to a less extent as a cattle feed, but in the Southwest and the Mississippi Valley their disposition was a problem. There are still laws in existence in some states prohibiting throwing them into the streams, because they rot and become deleterious to the fish. They could not be piled out in the weather, because they would rot and give off an unpleasant odor, so it became a difficult matter to know what disposition to make of them. And today there are hundreds of millions of dollars invested in plants using the cottonseed as a raw material, and this is the second largest manufacturing industry in the southern states. It is not, however, confined to the southern states, for most of the large refineries producing the finished products are located in the big cities of the East and Middle West. Hundreds of chemists have made this little cotton seed their life study, and it is entirely through the science of chemistry that the industry has been developed.

Herewith is a chart showing the principal products made from this little seed. There are numerous combinations with other products that are not given on this chart.

CHART SHOWING THE PRODUCTS OF COTTONSEED



Chemistry of the Cottonseed

Cottonseed chemistry should be divided into four main divisions: chemical control of oil mills; determination of quality through chemical analyses; chemistry of animal nutrition, or feeds for cattle and live stock; and chemistry of edible products for human consumption.

Chemical Control of Crude-Oil Mills

A good oil miller wishes first to determine the quality and composition of his raw material and the price which he can pay for it. This is accomplished by testing the cottonseed in the laboratory. Four tests should be made: quality, moisture, oil, and nitrogen. The test for quality is simply grading the seed, which can be done by an expert who can tell from the color of the kernels whether they are prime or off-grade. The moisture shows the amount paid for water in purchasing the seed, and also whether they will keep in storage for any length of time. If the moisture is more than 10 per cent it is dangerous to store them. The oil determination shows what yield a mill may expect from a ton of seed. The oil is the most valuable part of the seed and those containing a high percentage of oil are worth more. The nitrogen determination permits a calculation to be made showing the yield of meal and its approximate protein content.

The manufacture of crude oil begins when the seed are unloaded from a wagon, truck, or car into a screw conveyor, part of which has a screen bottom to allow the sand and small foreign matter to be eliminated before the seed go into the mill. The seed then go

through cleaning machinery, and from there to the linters or gins where the short fiber is removed. This fiber is the linters on our chart, page 78. From this machinery the hulls go into a machine known as the huller, where they are cut by knives or sharp blades, dropping directly onto shakers where the kernel and the hulls are separated as completely as possible. The hulls then go into beaters where any fine meats that are left by the shakers are recovered. These fine meats go with the kernels to heavy steel rolls through which they pass, the oil cells being broken.

The meats next go to the cookers, where they are cooked by steam under pressure until in proper condition for pressing, when they are wrapped in hair presscloth and put into hydraulic presses. These presses develop a pressure of from three to four thousand pounds per square inch and by this method the crude oil is forced out of the meats and a hard cake left. The oil passes on to the storage tanks and the cake goes to an attrition mill, where it is ground into meal.

An up-to-date miller draws frequent samples for chemical tests. The hulls are tested for fine meats and oil content to show the manufacturer whether his machinery is getting all the oil and meal from the hulls that it should. The meal or cake is tested to determine how much oil is left in the cake, and a nitrogen test is also made to determine the protein quality of the meal. Seeds vary considerably in nitrogen content, and this results in a variable protein content of meal. As the meal is sold almost entirely on its protein content, it is necessary for the miller to know, and if possible to regulate, his grade of meal. No mill can be successful unless the laboratory forms an important part of its organization.

Determination of Quality through Chemical Analysis

Cottonseed products are sold on quality, as determined by chemical analyses. This applies to the lint, hulls, meal, and oil. Tests on lint and hulls are seldom required, their grade depending more upon physical characteristics. The meal is tested for its fat and protein content, its value being based on this composition. The oil is tested for its free fatty acid and loss in refining, or shrinkage when producing a refined oil from the crude. The refined oil is then graded as to color and flavor. The laboratory refining test is made by the use of caustic soda, the strength of which is calculated from the free fatty acid content of the oil. The crude oil is treated with this caustic soda solution and stirred slowly while slight heat is applied until a separation takes place between the foots and the yellow oil. The foots carry down the foreign matter and are known in the trade as soapstock, the uses of which are shown on the chart, page 78. The refined or yellow oil is decanted off and filtered. The grade of the oil is based on its refining loss, color, odor, and flavor. The trade has certain requirements which are given in the trade rules of the Interstate Cottonseed Crushers' Association.

While cottonseed meal is used in some sections extensively as a fertilizer on account of its nitrogen content, its principal and most economic use is for cattle and stock feeding. As this is a very concentrated protein the feeder should obtain the advice of an expert as to how it should be fed. Chemistry here plays a most important part, as all the experiments and tests are made jointly through the Department of Animal Husbandry and the laboratory. For those in-

terested in this phase of chemistry probably the best and most practical book published is "Feeds and Feeding" by Henry and Morrison of the University of Wisconsin.

Cotton Products in Foods

The chemistry of edible products for human consumption deals mainly with the chemistry of the refinery and the lard plant, or what might be termed the finished products. By far the greatest accomplishments of the industry have been obtained in this department. Here the research chemist has great opportunity to give his imagination full sway and it is through him that cottonseed oil has developed into one of the greatest and purest edible products of the age. By far its greatest use is in the production of compound lard.

Crude cottonseed oil is purchased by the refiners in tank car lots, and is refined in large kettles using the same process on a large scale as described for the laboratory. The yellow oil is then heated with a small percentage of fuller's earth, which bleaches it almost water white. After bleaching, the oil is carefully filtered through fine cloths and absolutely all the earth removed. The oil then passes into a deodorizer where it is heated to a high temperature and washed with superheated steam. This removes any sources of odor that may have been left and the product should then be a tasteless, neutral oil of great purity. Sometimes the yellow oil is deodorized without bleach and this is used extensively as cooking or salad oil.

Lard compound is made by mixing the white oil with a small percentage of hydrogenated or hardened oil. This is melted and chilled on large steel rolls.

The chilled oil is then flaked off and goes into buckets, tubs, or barrels, and is sold as lard compound.

All of the refining methods and subsequent manufacture of lard compound, oleomargarine, butter substitutes, etc., are entirely results of chemical ideas and experiments. It can probably be stated without contradiction that the cottonseed products industry is more largely the result of chemical investigation than any of our other large industries. Hydrogenating or hardening oil is the latest and probably the most important of our recent chemical discoveries in the field of food production. This is such a broad subject that the student is referred to "Hydrogenation of Oils" by Ellis, published by D. Van Nostrand Company.

Work to Be Done

Now in view of the fact that the wonderful chemical developments of this industry have been accomplished in the last half century, it is natural to conclude that there is much yet to be done. There is probably no more fertile field in chemistry for research investigation. Some of the methods are still very crude and there are great economic losses which should be eliminated. To those who are interested in the real fundamentals of the industry the Book of Rules of the Interstate Cottonseed Crushers' Association, which can be obtained from the office of this association in Dallas, Texas, will prove of interest. It contains not only the trading rules but also the official methods of chemical analyses.

Those who are interested in higher chemistry or in that fairyland—research—will find in the chemistry of vegetable fats a wonderful field. To fire the imagi-

nation or whet the intellectual appetite of the scientist the insignificant and rather ugly little cottonseed will be found comparable only to Aladdin's lamp in the products which it will produce and the food for scientific research which it contains.

CHAPTER VI

CHEMISTRY IN THE ELECTRICAL INDUSTRY

BUCKNER SPEED

Technical Expert, Patent Department, Western Electric Co., Inc.

If we consider physics and chemistry broadly, it appears that physics may be regarded as the highly trained and discriminating use of the three senses of seeing, feeling, and hearing; while chemistry is occupied with finding out the inner qualities of things, such as those which the savage detects by the use of the senses of smelling and tasting. The trained chemist brings many pieces of apparatus into play to assist him in metaphorically tasting and smelling things.

The electrical industries are engaged in making electrical energy or power, transporting it elsewhere and making it do useful work, such as propelling a street car, lighting a lamp, or making a telephone talk; also in manufacturing the machinery and apparatus for making, distributing, and measuring these services.

Everyone will understand that the size, shape, and arrangement of the parts of an electrical machine influence the amount of useful work that can be obtained for a given expenditure. We know that car wheels must be round; that a heavy generator must have large bearings; and that the insulation of a wire must surround it completely. It is the engineer's job to decide the nice refinements of these matters of size, shape, and arrangement.

On the other hand, a choice must be made of the materials of which the parts of the apparatus are to be constructed. Some of the inner qualities of materials are very familiar, as, for example, that metals conduct or carry electricity while glass prevents it from flowing. However, between these extremes there are all gradations of the property of conducting electricity. All metals stop electrical energy to some extent, and all insulators allow some electricity to escape from the path intended for it. Therefore, the electrical industry also requires the trained sense of chemically smelling and tasting to determine the excellence and uniformity of the material which the electrical engineer arranges. For example, transportation of electricity has been greatly cheapened and improved by the removal of very small amounts of impurities from copper which is to be used for that purpose. Indeed, chemists have found that the conductivity of all metals is improved by making them very pure.

It really makes very little difference how intricate and roundabout the chemical method is by which a degree of acidity or the amount of impurity in a substance is determined; it only requires a little patience to trace the method back to its original form when it can be classified as smelling the object or biting and tasting it.

When we hear the words "chemical laboratory," we think of glass apparatus and balances, but it is really very surprising how accurate the simple, direct applications of the five senses may become in a highly trained person; for example, an expert tea taster who can recognize in a cup of tea the place where the tea was raised and the year in which it was picked; or an

expert French wine taster who can tell almost the side of the particular hill on which the grapes grew. There used to be an old phrase "as knowing as a miller's thumb." The miller determined the fineness and character of his flour by rubbing it between the thumb and forefinger. From this we also obtain the much despised phrase "rule of thumb." The miller was a physicist using his sense of touch; the tea taster and the wine taster are chemists in the broad sense.

The Chemist's Part

In the electrical industry the work of the chemist is partly inspection—the determination of the purity or uniformity of the materials of construction. It is partly control work—that is to say, the using of highly developed tests which take the place of the sensitive nose and discriminating taste of the cook in order to determine whether a particular batch of insulating varnish, for example, has become completely cooked. But no doubt the most attractive thing to the young student of chemistry who is thinking of entering the electrical industry is the chemist who is engaged in actually trying new combinations with the endeavor to discover and to invent new and useful combinations of things which are to become insulators, or conductors, or magnetic materials, or inert structural support substances.

In the electrical industry the chemist is likely to be dumbfounded at any moment by the peremptory demand to produce on the shortest notice a new substance which will have a combination of qualities hitherto unknown. For instance, a lubricant which will keep a bearing lubricated several years, will catch no dust, will not creep along the shaft, will not corrode, and

will not stick if the bearing has not been operated for several weeks—rather a man-size job! Or the chemist may receive an order to produce a variety of rubber that will be measurably fire-resisting, and that will stand light and moisture better than ordinary rubber. And he must do his job. He cannot reply that it is impossible, and consequently must be able, in case the direct answer is not within his power, at least to suggest some satisfactory method of doing something just as good; in the case of the rubber just mentioned, putting some sort of dressing on it which will protect it against fire, weather, and light.

Desirable Training

Both physics and chemistry merge into one, when the attempt is made to inquire into the ultimate elements of things, and a very beautiful philosophy has been developed around the electron theory of matter. This is a ravishingly fascinating subject to teach and to dream over, and frequently actually stimulating to the imagination to the extent of being able to evoke valuable thoughts and even invention. But it must not be forgotten that the chief training of a chemist, wherever his occupation leads him, finally must be the laborious acquirement of intimate first-hand knowledge of the smell-and-taste-like qualities of a vast number of things, not only elements alone but also the well-known combinations of them and particularly those occurring in nature. And so a well-trained chemist must know his geography first and how the geology of the world is distributed on the maps, and, further, he must know a great deal about the growing things of the world, where they come from, how they are obtained, and how they are shipped. Mere

learning of the principles of things would make his store of knowledge a meager one.

A Call to Chemistry

Are there great and outstanding problems of a peculiarly chemical nature in the electrical industry? Indeed there are. To begin with, we know far too little of the dependence of electrical conductivity on purity in metals, or in changes which may be imposed upon metals by which the undesirable impurities may be made less important. For instance, it is not beyond the justifiable hope of the chemist that he may produce a cheap substance, materially more conductive than present electric wires; nor that he may be able to produce a more highly resistive and more highly infusible substance than the present-day heating wires.

The whole subject of thermoelectricity, that is, the direct conversion of heat into electricity, is probably as much chemical as physical. This is a field that has lain dormant for many years so far as major discoveries are concerned.

The recent advances in magnetic materials, such as the vacuum-purified irons of Yensen, the unprecedentedly soft permalloy of Elmen, and the almost eternally permanent magnetic steel of Honda, are good examples of tremendous advances made in recent years in fields that had been thought to be barren of possibility.

The need for new chemical substances for varnishes, for paper, or other filmy material, methods of treating cotton or other fibers to improve their electrical or wearing qualities, for making mica substitutes and fireproofing methods, are all within the promise of the future chemist, and the need is a growing one in every case.

In common with many other industries, the electrical industry is a vast consumer of ordinary paints, lacquers, and varnishes for protective purposes, and not alone must the purchases of these materials be guided by painstaking chemical inspection but, when made within the electrical factory itself as a specialty, they must be made under highly skilled chemical control. But here again the chemist with a creative mind finds a wide field for the exercise of his imagination and a persistent energy, and out of intelligent inspection and control laboratories often come most valuable discoveries.

The chemistry of ordinary black carbon, much as it has been studied, has by no means been mastered from an electrical standpoint. We may now make carbons whose electrical resistance will diminish as they become warm, and other varieties of carbon whose electrical resistance will increase as they become warm, but there is still far to go in many other unexpected directions. Carbon is a wonder mine for the chemist who will work it.

Fine electric wires must be drawn through diamond dies. Substitutes for them are within the province of the chemist.

The development of automatic signals, relays, and switches has given rise to requirements for materials for springs—flat, spiral, crooked, of every shape—which must have such characteristics as nonrust, nonaging, and noneverything almost, coupled with many positive characters; and here the chemist may find a wide field. A great number of unexplained facts, possibly chemical or metallurgical, are surrounding the whole enormous question of springiness and hardness.

Much may even yet be done in getting better control methods for boiler-furnace combustion in power plants; chemical and physical chemical methods and apparatus are used to regulate the amount of air admitted to the furnaces. Already better economy and also smoke improvement have resulted from the efforts of chemists. Besides, the fuel itself must be analyzed and its heat units measured, often as a regular basis of purchase. And boiler water must be rendered sufficiently pure so that scale and mud will not deposit in the boilers; this requires applied chemistry.

The whole subject of corrosion, whether because of salinity of cooling water or from stray currents in the earth, takes chemists and good ones, men with imagination and detective-like ingenuity. It is not all in books! Not by a great deal. There is plenty of frontier for the wideawake chemist who is ready to enter the electrical field with the set determination to do all that is expected of him and *some more besides.* It is that "some more besides" that lifts him out of the humdrum into the responsibilities of executive position.

Electrochemistry is, of course, peculiarly an electrical industry, and so rapid has the advance been in the last few years in electrodepositing of unusual metals and the surprisingly valuable results obtained by them, that one would almost feel inclined to say that in electrochemistry lies the great field for the chemist engaged in the electrical industry, if it were not for the fact that in organic chemistry we are day by day turning out new substances which, almost before they are out of the test tube, are demanded in ton quantities for insulators and preservatives and lacquers.

No doubt the physicist would lay claim to a monopoly of further work in the field of the rare gases, such as argon and neon, which were discovered through the study of the density of pure nitrogen, in comparison with the supposed pure nitrogen prepared from air. These, until lately unknown gases, are now used in electric lamps and bulbs with great saving and profit. But the physical chemist will have his inning in this field in finding new methods of winning these gases more cheaply.

There is still an unsatisfactorily developed field of investigation and invention in methods and apparatus for direct refrigeration. Here is a wide field for deep-down imagination on the part of the young physical chemist, especially in the discovery and development of methods which will give us smaller and cheaper refrigerators than have yet been exploited.

How shall the high school or preparatory student, about to choose his college career, inform himself relative to the various electrical industries? Text books and discussions such as this one may not give the student the complete picture. He should also acquaint himself with the advertisements to be found in the technical, scientific, and trade papers of the electrical industry and the transactions of the electrical societies. These are usually available in the university or the public libraries of our larger cities and are frequently worth more for the advertising matter in their back pages than for their pages of text.

When a young man is seeking employment, he greatly appreciates a friend within the doors who will aid him in obtaining personal contact with the company which he is seeking to enter. There is this quality in a remarkable book written a few years ago by Elwood Hendrick under the title of "Every Man's

Chemistry." A student is led into the subject of chemistry (which he is supposed to have already studied) with a friendly hand, and told a great many interesting anecdotes about chemistry that stick wonderfully well and serve as acquaintance points on which to attach other knowledge as it grows. Many of the present-day works on chemistry are so formal and compressed and frequently intended to be used in the lecture room with the voice of the professor to explain and make easy, that they are very hard reading indeed. Such is not true of the older textbooks and, in particular, some of the original papers of the great investigators of the past. Faraday's "Memoirs" are almost ideal, both in conveying to the student the atmosphere of laboratory work of the highest character and also simplicity of expression coupled with the most searching thought. Some modern writers have seemed to write as if obscurity of expression lent dignity and profundity; it does not.

Importance of Broad Training

But, after all, the chemical student must accumulate in his head many facts before he can begin thinking very profitably. He must learn the qualities, the refinements of the smell-and-taste idea of things, the solubilities, the crystal habits, the acid or alkali behavior, and such like of a vast number of things. Visiting chemical exhibitions is well worth while, and as much acquaintance during vacations and otherwise with whatever chemical factories are within reach, is vastly valuable.

Probably no greater misfortune could happen to a young student than to attend a college which had unwisely put into its curriculum a course called

"Chemistry for those who intend to go into the electrical industry," because before the student would have finished such a course he would have circumscribed his knowledge to such an extent that he would prove of little value to the electrical industry.

A breadth of information, and consequently the ability to substitute one thing for another, and to have a more or less intuitive knowledge of and feeling for things, are great helps to the chemist in the electrical industry. Personally, I would feel that a man who had studied Greek for a year would be a little better chemist for it. Else, how will he know how to give a sounding name to the wonderful substance that he purposes to discover?

CHAPTER VII

SOME APPLICATIONS OF ELECTROCHEMISTRY

A. H. Hooker

Technical Director, Hooker Electrochemical Company

Some of the products that play an extremely important part in our daily life, so important that the very health and life of an entire community may depend upon them, have never been seen and are scarcely known even by name to the average person. Such, for example, is liquid chlorine.

Scarcely more than fifteen years ago Niagara Falls, the center of the chlorine industry, in fact of the electrochemical industry, was a veritable hotbed of typhoid fever owing to the water supply from the Niagara River being polluted by the cities above. The introduction of suitable filtration and the treatment of the water with chlorine changed this epidemic condition almost overnight, the hospitals were emptied of typhoid cases, and now typhoid is almost unheard of in the town. Within the past few years, hundreds of other towns and cities have adopted this practice of chlorine treatment for their water. Today, fully three-fourths of the water supplied to cities in the United States for household use is first chlorine-treated. The result is that an epidemic of typhoid in any community is a disgrace to the health authorities.

The amount of chlorine used is almost incredibly small. Less than one drop of chlorine to a fifty-gallon

barrel of water suffices to destroy the bacteria. This chlorine then becomes a mere trace of the mineral chlorides from which it was produced. A thousand times this amount would be harmless to human beings.

The raw material from which this chlorine is produced is sodium chloride, common table salt; the process is an electrochemical one. An electrolytic cell or tank constructed partly of concrete and partly of steel is used. In this are placed positive electrodes or anodes consisting of blades or rods of Acheson graphite (an electric-furnace product). These electrodes are suspended in a bath consisting of a strong brine, a solution of purified salt. The outer walls of this brine bath consist of a diaphragm or dense filter of asbestos which is used to regulate the flow and resist the action of chlorine-saturated brine. This, in turn, is supported by a perforated steel plate or screen, which acts as the negative electrode or cathode, and is electrically connected to an outside plate of steel. A group of these cells, connected in series, forms a circuit. When a suitable electric current is passed through such a circuit, salt is decomposed, or broken down by the electric energy, into chlorine and sodium. The chlorine separates as a gas at the anodes in the center of the cell, and the sodium is deposited on the steel cathode. This sodium when brought into contact with water immediately decomposes the water, producing caustic soda and hydrogen gas. Hence we have three products from the decomposition of salt and water as follows:

$$NaCl \text{ (salt)} + H_2O \text{ (water)} = NaOH \text{ (caustic soda)} + Cl \text{ (chlorine)} + H \text{ (hydrogen)}.$$

This simple reaction forms the basis of a great electrochemical industry centering around the produc-

tion of electrolytic chlorine, hydrogen, and caustic soda. Millions of dollars are invested in these plants, which require large capital outlay and thousands of horsepower of electrical energy to decompose salt. Owing to the large amount of power used and the proximity of Niagara Falls to a particularly suitable salt supply in western New York, as well as its central location for distribution, it was natural for Niagara Falls to assume and maintain the lead with several large plants for the production of chlorine products. Several other plants are scattered in different parts of the country and a few are operated in connection with pulp and paper mills.

The use of chlorine in water purification, important as it is to the community, takes but a small tonnage of the required production. Some is used directly at the producing plants as a gas for the manufacture of chemicals, more is absorbed by hydrated lime to form bleaching powder or chloride of lime for transportation, or liquefied by compression and refrigeration of the gas and shipped in liquid form in steel cylinders and tank cars for final use in the bleaching of wood pulp, paper, textiles, and shellac, either as calcium or sodium hypochlorite. In this latter form it is largely used in the laundries and as a household disinfectant. Other important uses for chlorine are the production of synthetic coal-tar dyes, chemicals, and pharmaceuticals, such as sulfur black, artificial indigo, anthraquinone, benzoic acid, benzaldehyde, benzoate of soda, chloroform, carbon tetrachloride, sulfur chloride, in the cracking of oils to produce gasoline, in the purification of oils to remove sulfur; in the production of zinc chloride, for the preservation of timber and railroad ties; in the extraction and purification of metals from ores; as the base of all the important war gases,

such as phosgene, mustard gas, and chloropicrin; for the production of picric acid and dinitrophenol, alike useful as dyes and as explosives; for the production of an extremely pure muriatic acid; for insecticides like para-dichlorobenzene (Paracide), used for the peach borer and the household moth, and calcium arsenate for the cotton boll weevil. Thus chlorine enters our daily life quite unexpectedly through a hundred doors.

What is true of chlorine is true of many other electrochemical products, which are closely woven into our daily lives—often the more common and lowly the product the greater its real importance. Take the source of our chlorine, sodium chloride. A pinch of salt we hold in little regard, yet many of the nations of Europe have found that by taxing table salt they have hit upon a necessity which all must have, and from which a sure income can be drawn from the poor and the rich alike. In Italy and Germany it is as great an offense to extract tax from sea salt for household use as to extract tax from alcohol made from grapes, and in Germany the writer found the chemical plants using tax-free salt denatured with coal dust under government orders to prevent its use for household purposes.

As an example of this interrelation of certain electrochemicals on the materials of everyday life, let us take the relation of the electrochemical industry to a pair of cotton stockings. Possibly some one will suggest that cotton stockings are not a commonplace article, that the stockings of this generation are not made of cotton but of silk. Here, again, appearances may be deceptive for it is quite true that all the silk stockings worn today are not made from cotton—some are made from wood fiber—but to return to our subject. It has been shown that the electrochemical decomposition of common table salt and water gave three products—

chlorine gas, caustic soda, and hydrogen gas. This hydrogen gas can be burned with chlorine and will produce an extremely pure muriatic acid (HCl).

It can also be combined, using a nickel catalyzer with a soft oil like cottonseed oil, and will produce a lard-like compound such as cottolene.

This hydrogen can also be burned with air and the oxygen combined with it to produce water (H_2O). After freezing out the water, nearly pure nitrogen gas will be obtained. If this nitrogen gas, mixed with hydrogen gas, is passed through a special catalyst under conditions that will produce a very high heat and pressure, the nitrogen and hydrogen will combine to produce synthetic ammonia (NH_3)—still a gas. The pressures commonly developed where these gases are combined are extremely high—the German Haber process is operated at nearly 1000 atmospheres or 15,000 pounds pressure to the square inch; the Italian Casale process, using the hydrogen from the plant with which the writer is connected at Niagara Falls, uses less than one-half this pressure, but in order to be safe still requires a reaction chamber with the strength of a cannon. This ammonia gas can be cooled and liquefied by pressure and refrigeration as in the production of liquid chlorine. The product is anhydrous liquid ammonia, which is shipped in iron cylinders and used largely in refrigerating machines.

Another and far greater use for synthetic ammonia, particularly the development which has taken place in Germany since the World War, is in artificial fertilizers chiefly as sulfate of ammonia. The distribution of fixed nitrogen as a fertilizer in the form of ammonia should develop largely along another line in the United States. We are particularly favored by Nature in our deposits of phosphate rock. If this

phosphate rock be heated with sand and coke in an electric furnace, phosphoric acid can be separated from the impurities of the rock. If this phosphoric acid be combined with synthetic ammonia, two important elements of plant food, phosphoric acid and ammonia, result. This plant food or fertilizer, a product of the electrochemical industry, can then be shipped to the sandy cotton lands of the South as fertilizer for our cotton. As the cotton plant develops it is subject to destruction by a small beetle known as the cotton boll weevil. This insect pest must be destroyed if the cotton crop is to come to maturity, and again use is made of the chlorine produced from the electrolytic cell. This chlorine is absorbed in lime and forms chloride of lime or bleaching powder. Arsenic, when treated with this bleaching powder, is oxidized from arsenious to arsenic acid, and a combination known as arsenate of lime is formed which is used as an insecticide to kill the boll weevil.

Cotton is separated from the seed, is sent to the mill, and made into cotton thread. This must be bleached, and in order to bleach the cotton use is made of the electrolytic chlorine, which has been converted by refrigeration and pressure from a gas to a liquid, transported in cylinders, and then reëvaporated and absorbed in a solution of caustic soda, also a product of this electrolytic cell. We now have sodium hypochlorite, the bleaching solution used for cotton fabrics. In order still further to improve the cotton thread and give it a more glossy and silk-like appearance, it is mercerized by treatment with a strong solution of electrolytic caustic soda. The cotton is now white, but a black product is desired, so we turn again to electrolytic chlorine. If it is passed into coal-tar benzene, a liquid that has the general appearance of gasoline, and

some of it combined with the hydrogen from the benzene, hydrochloric acid is produced, the remainder of the chlorine forming a product known as monochlorobenzene. If this is treated with nitric acid, a further product, known as dinitrochlorobenzene, is obtained. If this, in turn, is treated with lime the chlorine separates as calcium chloride and a product known as dinitrophenol results. Dinitrophenol when treated with sodium sulfide becomes sulfur black, one of the most important black coal-tar dyes. This dye makes a very permanent black for our cotton stockings.

But it is desired to have a fancy clock of golden yellow on the side of the stockings, so we again turn to the South and find that when the cottonseed was cleaned before crushing and pressing to extract the oil there was some fine cotton fiber on the outside of the seed. This, when collected, is known as cotton linters. These cotton linters are sent to a paper mill, boiled in a digester with caustic soda, bleached with a solution of the electrolytic chlorine and lime, and converted into a beautiful white blotting paper, the basis for an artificial silk. The electrolytic furnace supplies another raw material. Sulfur and charcoal, when subjected to the heat of the electric furnace, combine to form a vile-smelling, heavy, volatile liquid known as carbon disulfide. This liquid will unite with caustic soda to form a compound known as sodium xanthate. Blotting paper made from cotton is soluble in this compound and produces a sirupy substance. This is passed through steel plates having holes finer than the finest cambric needle and comes out as little silken threads known as viscose artificial silk. It is desired to dye these threads a golden yellow, so the dinitrophenol made from the monochlorobenzene that was used to produce the sulfur black dye is again employed. If

this dinitrophenol is treated with strong nitric acid it is converted into trinitrophenol or picric acid, a product that is alike used as a yellow dye and as one of the most important high explosives. A yellow artificial silk for the embroidery on the side of our black cotton stockings is thus produced. The oil extracted from the cottonseed when combined with electrolytic caustic soda will produce a soap to wash the stockings.

Thus, in brief, we have the story of the relation of the electrochemical industry to a pair of cotton stockings.

CHAPTER VIII

CHEMISTRY IN THE FERTILIZER INDUSTRY

R. B. Deemer

Assistant Biochemist, Soil-Fertility Investigations, Bureau of Plant Industry, U. S. Department of Agriculture

While the fertilizer industry as such has had its birth and development within the past seventy-five or eighty years, the use of various materials as an aid to crop production is of much older origin. Thus, from the earliest recorded times, manure, animal refuse, bones, and fish were all applied by the ancients to the soil in farming. Even the Indians taught the early settlers of this country to drop a fish into each hill of corn that they planted. Whether these pioneers appreciated the agricultural value of these materials is doubtful, but it is certain that the principles underlying their beneficial results were not then known.

In fact, it was only very recently, somewhere near the middle of the eighteenth century, that chemists revealed to the world that plants require substances for their growth which, popularly speaking, may be termed foods. Just as man must eat to live, so must the plant in order to grow take into its system certain elements, as they are called by the chemist. Later, most of these elements were shown to be mineral; that is, such as are supplied by the soil. However, like some of our people who are unable to afford a balanced ration for their families, many of our soils, particularly after

many years of cropping, are unable because of poverty to provide all of the essential elements. To enrich these soils so that they will again become productive, fertilizers which contain the lacking elements are supplied. Not only are exhausted soils thus made to increase their yields but many soils which are naturally too impoverished to produce good crops may be brought into a state of fertility through the use of fertilizers.

It has been more than three-quarters of a century since the principle underlying the use of fertilizers was first made known, yet much remains to be learned about the effect of fertilizer constituents upon plant growth. Your state probably has several chemists engaged in the study of some phase of this important question since there is an agricultural experiment station, and sometimes more than one, in every state of the Union. Our Federal Government also maintains a staff of experts studying many of the important features of this interesting and intricate problem. That the results of these studies are vital to the nation as a whole and to every individual will be realized when you recall what a deciding factor food supply was to ourselves and to our Allies during the World War.

Fertilizer Constituents

Of the many elements entering into the composition of the plant, the fertilizer industry is concerned at present principally with three, although there are others that are assuming importance. The first of these elements, potassium, is supplied to the purchaser in the form of mineral salts, some of which are similar in appearance to our common table salt and are readily soluble in water. The manufacturer uses the term pot-

ash to refer to either the element or the salt in which it is present. Phosphorus, another of the elements in which we are interested, is probably familiar to the older of us as an ingredient of matches, although the modern match no longer contains it as the element. It is generally supplied to the user of commercial fertilizers in the form of acid phosphate. The term phosphoric acid is used universally by the trade when speaking of phosphorus fertilizers. Nitrogen, the third member of this highly important group of plant foods, is obtained from two sources: namely, the animal and plant kingdoms and the mineral kingdom. The form in which the nitrogen is contained in these sources is quite different and so the term organic is applied to the nitrogen derived from the animal and plant kingdoms, while that supplied by the mineral kingdom is designated as inorganic. Materials such as tankage and cottonseed meal are carriers of organic nitrogen; and mineral salts, such as Chile saltpeter, furnish the inorganic nitrogen.

The fertilizer manufacturer utilizes these various sources of raw materials in the making of fertilizer. He mixes them in the proportions best suited to the needs of the soils and the particular crop to which they are to be applied, and sells the mixture to the consumer. The fertilizer industry is based on chemical principles, and the products which it produces, we shall learn, are essentially chemicals that require the attention of the chemist, just as much as do the drugs and medicines which you purchase from your druggist. To carry the illustration a little further, the fertilizer manufacturer, like the druggist, compounds mixtures from different materials, many of which are supplied in both instances by the chemist.

Beginning of the Fertilizer Industry

The chemist showed that materials such as bone did not contain their fertilizing elements in a form that could be readily taken up by the plant, and suggested a treatment that would make them soluble in water and hence assimilable by the plant. He proposed the treatment of bone, which contains phosphorus, with a strong acid, known to the layman as oil of vitriol, and as sulfuric acid to the chemist. Truly remarkable results on the rate and amount of plant growth were obtained by the use of this treated bone. Natural phosphates, known as rock phosphate, were later substituted as a source of the phosphorus, and the product obtained by treatment with sulfuric acid became known as acid phosphate.

Acid Phosphate

The discovery, in 1862, of large deposits of natural phosphates in South Carolina, soon induced capital to start the manufacture of this fertilizer ingredient in America. Figures are, as a rule, dry reading but in this instance they may help to impress upon you the importance of this product, the result of a chemist's work. The tonnage of acid phosphate produced in this country alone in 1922, a year taken at random, was over three-quarters of a million tons.

Every art of the chemist has been used in advancing this branch of the fertilizer industry. The acid phosphate maker at first required only three sheds for his plant: one to cover the untreated phosphate; the second, a den in which to treat his mixtures; and a third in which to store his product. Harrows, hoes, rakes, and a screen were all the tools that he used. His mix-

tures, portions of which were sent away to a chemist for analysis, were made by trial. The acid phosphate resulting from such hit-or-miss methods often caked and "set" before mixing was complete. Today his plant, which is designed by a chemical engineer, contains a network of modern machinery, and every step of the process is subject to the immediate supervision of a chemist working in a modern, well-equipped laboratory at the plant. This backbone of the fertilizer industry is sold on a quality basis, determined by chemical analysis, and is as near perfection as is practically possible.

The research chemist has been indispensable to the manufacturer of acid phosphate. Iron and aluminium occur in excessive amounts in the natural phosphates of this country and are a serious hindrance to the production of high-grade acid phosphate. Although the ingenuity and resourcefulness of the chemist have overcome to a great extent their harmful effect, there are, nevertheless, mined and thrown away approximately two tons of rock phosphate for every ton of marketable phosphate produced. The elimination of such an enormous waste of our phosphate reserves would mean an untold saving to the fertilizer industry.

The revolutionary results of the chemist's art are strikingly illustrated in the manufacture of the sulfuric acid upon which the production of acid phosphate depends.

Like most of our acids, sulfuric acid is made from crude materials. Through the laborious efforts of an alchemist, before chemistry became a science, this acid was first produced from sulfate of iron, also known as green vitriol and probably more familiar to the reader as copperas. The method which he devised, or

at least the principles involved, is still in use at Nordhausen, Saxony. It was through a second achievement of this same alchemist that a method more suitable to large-scale production was developed. He burned sulfur under a glass bell-jar suspended over water, and from this simple beginning there resulted a procedure which, from the large lead chambers now used in place of the simple glass bell-jar, has become known as the chamber method. It was long the most profitable method of production. Step by step this process was improved until there now seems to be little that can be done to increase its efficiency.

A strong competitor of the chamber method has appeared in a recent process based on principles quite in keeping with present-day speeding that is rampant. Platinum, the metal so much valued by the ladies as jewelry, possesses the property, first noted by a chemist, of speeding up some of the chemical changes which occur during the production of sulfuric acid, and as a result of the use of this metal much less room is required than in the chamber process. Consequently the economies resulting from the use of smaller plants have enabled the method to jeopardize seriously the supremacy of its rival. The future of the contact process depends a great deal upon the services of the chemist. There occur with the raw materials other substances which, when they come in contact with the platinum, literally poison it and sap its vitality so that it is no longer able to do the work required. It is these intruders that the chemist must grapple with and vanquish. Also the soaring price of platinum makes it imperative that the chemist develop new sources of these catalysts, as he calls them, so that the ladies may continue to adorn themselves.

It is said that "money talks." Perhaps a better realization of the tremendous strides made by the chemist in the advancement of the methods of sulfuric acid manufacture from simple beginnings to the present industrial importance may be had by considering the decline in the price of the product. Each improvement in the process of manufacture has resulted in a decreased cost. The original process of the alchemist produced a product that sold for about one dollar and a quarter an ounce; his first improvement reduced the price about one-half for approximately sixteen times this quantity. Later developments brought the price down still further until a pound could be purchased for about twenty-five cents; and more recent developments have resulted in such economies that at present we can obtain a pound of sulfuric acid for less than a cent.

Potash

Until quite recently Germany was practically the world's sole source of potash. Her supply is secured from immense deposits of ocean salts. It is supposed that these deposits were formed by the shutting off of a large arm of the sea. Through evaporation, subsequent refilling of the basin by the tide, and continuation of this process large beds, often 5000 feet in depth, of potash-bearing salts were accumulated. In 1915 there were 190 mines in Germany, 40 of which could easily supply the world with potash.

Two countries have succeeded in freeing themselves from this monopoly: one, directly through the efforts of her chemists in a chemical achievement of the greatest brilliancy; the other, indirectly through the efforts

of her chemists during the World War. The first of these countries is Italy. She has a large supply of a potash-bearing mineral and, while the fertilizer element which it contains is in an insoluble form, an Italian chemist has shown that it can be rendered available to the plant by a simple chemical treatment. Nature usually likes to make us wring her treasures from her and this instance is no exception. Although the treatment of the potash-bearing ore is a simple one, the successful development of the deposits was greatly hindered by the presence of a troublesome bedfellow—a mineral with magnetic properties. In fact, if the chemist had not persisted and been successful in his efforts to rout him out, it is doubtful whether this new source of potash would be of economic importance. With patience and perseverance this Italian chemist undertook to solve the difficulty and soon became convinced that the result could be accomplished by the use of electromagnetic methods.

The Germans have been very successful in applying this type of method in other industrial processes and so they were asked to study the difficulties involved in this instance. They reported that the ore would not yield to the treatment that it was desired to apply. The Italian chemist was not convinced by their report and so determined was he to give to his country this treasure—more priceless than jewels—that he persisted with his experiment until he overcame all obstacles. His method is a commercial success and Italy now no longer need depend upon imported potash for her crops.

Some of the richest and largest potash mines of Germany were located in Alsace-Lorraine and by regaining this territory France, the second country to secure an independent source of potash, has assured herself

an adequate supply for all her own requirements and a considerable quantity for export.

America has almost an unlimited supply of phosphates and a process for rendering them suitable for fertilizer mixtures. On the other hand, while we have probably a more inexhaustible source of potash in our many potassium-bearing rocks, we have as yet no economical method with which we may unlock the doors of Nature's storehouse and secure her treasure. Like the phosphorus of the phosphates, the potassium of these reserves is insoluble and must be treated in some way to make it more readily available to the plant. During the World War we spent some fifty million dollars in this country in an attempt to solve the difficulties of producing potash in a marketable form, and as yet relatively little has been accomplished. Government chemists have shown that the cement plants and blast furnace industries together produce annually about one hundred and seventy thousand tons of potash as a by-product dust in their gases. A small part of this potash is being recovered, and more may be saved eventually, but some of it may never pay the expense of recovery. Brines and lake deposits in the West proved a profitable source of potash during the war and some of these are still being worked; but generally the process of treatment is too expensive to compete with foreign potash. Chemists successfully treated seaweed during this period of excessively high prices and curtailed supply and obtained a considerable amount of potash from this source. However, the process which was developed was unable to survive when these abnormal conditions no longer prevailed. Very recent reports from development wells in the oil fields in the Southwest indicate that there may be some hopes of locating in this region natural

potash deposits containing potash salts similar to those of Germany and France.

Edison, by persevering against what must have seemed to him in his younger days insurmountable obstacles, later succeeded in giving to the world the electric light. You will agree that it is one of the greatest achievements in many centuries. He has given light and comfort to countless millions groping in the dark. The research ultimately leading to the method that will produce potash from our inexhaustible deposits of natural potassium-bearing minerals should prove as fascinating to some future chemist of this industry as Edison's researches must have been to him. The overcoming of this difficult problem should appeal most intensely to the American chemist also from the patriotic viewpoint. Present methods and future developments of modern warfare make it almost certain that foreign sources of potash will be cut off if we are involved in a war. While the last war raged in all its fury those responsible for the successful conduct of the affairs of the nation soon realized the importance of the food problem confronting our people and our Allies. Most of us can recall the appeals that were broadcasted throughout the land to the farmer beseeching him to increase his food crops to the limit.

That plants suffer from the lack of potash was brought forcibly to the attention of the farmer during the shortage of this fertilizer ingredient. The potato growers of Maine were confronted with a disease that devastated their crops at a time when they were most needed. Here, again, a government chemist showed the trouble to be due to the missing potash in the war-time fertilizers. The plant was literally starved

Courtesy, Soil Fertility Investigations.

Diseased Plant. Fertilizer Containing No Potash.

Courtesy, Soil Fertility Investigations.

Normal Plant. Fertilizer Containing Potash.
Illustrating the effect of the lack of potash as observed in the study of "Potash Hunger" on the potato.

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for potash. This diseased condition induced by the lack of this plant food has become known as "potash hunger."

Nitrogen

Though surrounded by an atmosphere containing a high proportion of nitrogen, the plant cannot utilize this element as such. Consequently the manufacturer supplies this third fertilizer ingredient in a more acceptable form. It has been some fifty-four years since the establishment of the fertilizer industry, and its growth and expansion for the first thirty years was gradual; but from then on it grew by leaps and bounds, until today it is the largest heavy chemical industry in America. When the age of this young giant had reached the half century mark the result of his labors was a product valued at considerably more than a quarter of a billion dollars. The total tonnage of this enormous output at that time was over eight million tons. Since approximately three-fourths of the mixed fertilizers produced contain nitrogen in some form, we can easily see what importance the nitrogen question assumes. At the present rate of increase in production it is estimated that in 1930 the output of commercial fertilizers will have reached over fifteen million tons. It is believed that there will be introduced into these mixtures 315,000 tons of nitrogen, about five-sixths of which will be derived from inorganic sources. At present the source of this form of nitrogen is chiefly nitrate of soda or Chile saltpeter, some sulfate of ammonia, and cyanamide.

Chile saltpeter is the world's chief supply of the inorganic form of fertilizer nitrogen, but immense as

the deposits are they are not inexhaustible. Furthermore, there is much for the chemist to do to improve the present method of production of Chilean nitrate salts. Sulfate of ammonia is obtained chiefly from gases that used to be allowed to go to waste in the production of coke. These gases contain a considerable quantity of ammonia gas. Ordinary household ammonia is water into which ammonia gas has been passed. If we first introduce some sulfuric acid into the water and then pass in the ammonia gas, we obtain in solution the product which appears on the market as sulfate of ammonia. The chemist by such simple means has added a very valuable source of nitrogen to our supply.

Cyanamid represents chemistry's tapping of an inexhaustible source of nitrogen, namely the air. The lime carbide with which we used to pack our bicycle lamp is today serving as one of the essential raw products of this industry. The chemist found that by proper inducement this familiar solid will capture and retain nitrogen gas when the two are brought into the presence of each other at a high temperature. There are several other processes for obtaining nitrogen from the air in a suitable form for use as a fertilizer. These are being operated abroad, but in this country the fixed nitrogen industry, as it is called, is largely dependent upon the method that produces Cyanamid. This industry is in its infancy and the field for research is unlimited. The direct combination of atmospheric nitrogen with hydrogen to form ammonia by means of catalyzers, as illustrated in connection with the production of sulfuric acid, and the direct oxidation of atmospheric nitrogen by its boon companion oxygen, areal play fellows that will not unite

until electrocuted, offer untold opportunities to the chemist to enrich further our supply of nitrogen for agricultural purposes. Since electricity is essential to effect these combinations we are thus taught to utilize to the nation's best advantage our countless millions of horsepower produced by such waterpower sites as Muscle Shoals.

All the nitrogen that is used in fertilizer mixtures is not derived from inorganic sources for at present about half of it is obtained from organic materials such as cottonseed meal, blood and animal tankage. Garbage tankage, fish scrap, hair, horns, and scrap leather are also used to a considerable extent. The last three of these materials must first be submitted to chemical treatment before being used as nitrogen carriers. Some of the organic sources of nitrogen are fast disappearing from the market of the fertilizer mixer. The chemist has stepped in to develop a supply of this form of nitrogen and has been partially successful. As a result of a process which he has helped to develop, some of the large cities are treating their sewage by chemical and bacteriological means which render it innocuous and available as a nitrogen carrier for the plant. The nitrogen in the resulting product is being studied to determine whether in this combination it is suitable as a fertilizer, and while as yet the results are incomplete they are very encouraging.

Dependent as we shall most probably be in the future upon inorganic nitrogen sources, there is an unlimited opportunity here for the research of the chemist who should seek to produce from these inorganic materials either nitrogen compounds that can fully take the place of our organic nitrogen or endeavor to reproduce the type of nitrogen compounds which

occur in organic materials such as cottonseed meal, blood, and tankage.

Fertilizers of the Future

Chemists are now striving to perfect a method for the treatment of phosphates which will give us our phosphorus, not as acid phosphate but in the form of a concentrated acid. If this new method should prove to be commercially feasible, fertilizer production might be entirely altered. This phosphorus carrier may be combined with potassium and ammonia in such a manner that we shall have a mineral salt, containing all three of these elements, as a sole source of fertilizers. The concentration of our present-day fertilizers is reduced by their content of inert materials, but the proposed fertilizers would be very concentrated water-soluble salts undiluted by other substances.

It is possible to use strychnine as a heart stimulant if taken in sufficiently small doses, but larger quantities cause death. Likewise, the plant may be stimulated and made to thrive upon moderate quantities of fertilizers, but an overdose is fatal. The mixtures which are the result of practices prevailing in the industry at present are such that the proper application can easily be regulated. With ordinary care in their use, injury never results; but with the more concentrated salts of the future we will be confronted with the problem of either diluting them or else using them in some way so that they will not injure the seed or the plant. Economic conditions of fifty or a hundred years from now will demand that we ship our fertilizers in as concentrated a form as possible and it

would seem, therefore, that our only hope lies in finding a means of using them without injury to the plant. The accomplishment of such results is not at all impossible. If the next forty years produce as many developments of a chemical nature as have the past forty years, we might even conceive that the chemist will be producing our fertilizers in such a form that they may be wafted or sprayed over the field from the cockpit of an airplane. It is impossible to predict fully future developments but we are certain that the borderland of this highly fascinating realm of unexplored possibilities has only been penetrated. In this search the American chemist no longer looks to the chemists of other nations for leadership, rather they are looking to America.

It is to the younger generation, to the chemists of tomorrow, that we must look for men who will maintain this leadership. The young chemist must prepare himself to receive the torch of leadership, now grasped by the present generation, and by his science, art, and skill complete the process of making America as free from the chemical dominance of other nations as our forefathers made it independent of political and moral dominance. In this there devolves upon the young chemists of America a duty graver and of more consequence than he who is not a chemist can appreciate. For, strange as it may appear, the political freedom of a nation will in future depend, in a large measure, upon its chemical independence, and this because, either rightly or wrongly, modern chemistry has so wrought that only those nations which excel in the arts and science of chemistry can excel in the arts and science of war. Thus a fertilizer factory which today, in peace, but supplies an element needed in our

soils and thus insures a more bountiful yield, may tomorrow, in war, supply a munition needed for our defense and thus insure a more efficient army.

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CHAPTER IX

INDUSTRIAL GASES

Clark S. Robinson

Department of Chemical Engineering, Massachusetts Institute of Technology

A great many years ago people, or rather people who thought about such things, believed that the universe was made up of four basic elements—earth, air, fire, and water. The various substances which we find upon the earth were supposed to be made up of combinations of these four elemental substances in the proper proportions. The term "air" was used in a very general sense and had no reference to the two gases of which today we know that our atmosphere largely consists. At that time the idea of a gas as a separate chemical substance did not exist. At a later period, in the Middle Ages during the time of the alchemists, it was the fashion to try to discover the means for changing lead and other common metals into gold. Experimenters in the monasteries and universities mixed all kinds of substances and heated them in their furnaces and retorts. Among the results of these investigations was the discovery that there were apparently a number of different kinds of air. Some of these varieties were harmless or good gases. Others were harmful and therefore bad gases. Many of our common industrial gases were thus discovered and some of their properties studied. It was not until a little over a hundred years ago that the true charac-

ter of gases was realized and an opportunity afforded for their use in the chemical processes responsible for our recent industrial development.

About the time of the Revolutionary War it was believed that when a combustible substance burned it lost to the air a substance called phlogiston, and that the flame given off during the burning was the phlogiston escaping. No one seemed to bother about where it went, but it was noted that when such a substance had been burned the air present was not capable of supporting further combustion and that it had also become incapable of supporting animal life. This remaining air, which we now call nitrogen, was therefore given the name of dephlogisticated air. People had never heard of oxygen at that time. It was noticed that when a metal such as iron was treated with an acid like sulfuric acid, a gas was given off which we now know as hydrogen. They noticed that this gas burned with a flame and left nothing behind it, so they called hydrogen, phlogiston, and the more experiments they performed the worse the confusion became until the classic experiments of Priestley, who identified oxygen and opened the door to our modern knowledge of what gases really are and what purpose they serve.

Our two most common gases are nitrogen and oxygen, the chief constituents of air, which consists of about one-fifth oxygen and four-fifths nitrogen. They are also our most important industrial gases—nitrogen as a basis for fertilizers and explosives, and oxygen for purposes of combustion.

Nitrogen

Nitrogen gas is very inert chemically. It dislikes to associate with other elements and does so only under

compulsion, retiring into its elemental condition under the least provocation. But since our food and clothing depend upon a satisfactory supply of this most important substance, it requires considerable effort on our part to put it to work or to "fix" it.

The United States produces some five billion bushels of wheat, oats, and corn annually, and it is computed that each bushel requires about 0.9 pound of nitrogen in order to grow it. This means that the soil of this country loses about 2,250,000 tons of nitrogen each year. If this loss is not made up by the use of fertilizers or by the planting of nitrogen-fixing crops, the soil will gradually become exhausted and fail to produce our food.

There is plenty of nitrogen available in the air for this purpose, as each square mile of the earth's surface has over it in the atmosphere more than twenty million tons of nitrogen. The use of some of this for fertilizer purposes does not deplete it because the nitrogen eventually finds its way back into the air after it has fulfilled its duty in the fixed condition. But it is very expensive to fix this gas. There are a number of ways of doing it and except for the use of nitrogen-fixing or leguminous crops, all require the use of electricity.

One method is to pass air through an electric arc. This causes some of the nitrogen to combine with the oxygen so that it can be absorbed and turned into nitric acid and nitrates. In 1921, 36,000 tons of nitrogen were fixed in this way.

Another method uses nitrogen, which has been separated from the oxygen of the air by liquefying and distilling it, and hydrogen, made by decomposing water. These two gases are combined under high temperature and pressure to form ammonia, which with sulfuric acid gives ammonium sulfate, and with

nitric acid, ammonium nitrate. In 1921 over 300,000 tons of nitrogen were fixed by this method.

Still another method uses nitrogen, obtained as in the previous method, and treats it with calcium carbide, the substance that is used in bicycle lamps to make acetylene light. This forms a substance called cyanamide, which may be used as such for fertilizer, or may be converted into ammonia or any other of the nitrogen compounds. About 325,000 tons of nitrogen were made into this material in 1921.

Nitrogen that has been stored in coal underground may be recovered in the form of ammonia by heating the coal in retorts, as is done in making illuminating gas. And in South America there are large deposits of nitrate of soda which are mined and shipped to this country. The combined nitrogen from these two sources used in the entire world during 1921 was nearly double all that obtained from the air by the electrical methods previously noted. These two sources are limited, however, and as they are depleted it will become more and more necessary to turn to nitrogen fixed from the air for the nitrogen in our fertilizer.

Oxygen

Oxygen is another of our important industrial gases, used chiefly for its property of oxidizing combustible materials for heat. For this purpose it is almost always used directly in the form of air. This has, however, certain disadvantages. The value of a fuel depends largely on the temperature that can be obtained with it; the hotter the fire, the more valuable is the fuel. When air is used as the source for oxygen, it is necessary for all the nitrogen that is associated with it to be heated in the combustion. This requires

a large proportion of the available heat, thus keeping the temperature down where it would otherwise go very much higher. Therefore the use of oxygen free from nitrogen permits very much higher temperatures.

In 1909 there were produced in the United States about four million cubic feet of oxygen, while in 1919, ten years later, over one billion cubic feet were produced. This tremendous increase was almost entirely due to the development of oxyacetylene cutting and welding of metals on account of the very high temperature produced by the oxyacetylene flame. This oxygen was produced partly by the liquefaction of air and its fractional distillation, giving nitrogen as a by-product, and partly by the electrolytic decomposition of water, which gives hydrogen as its by-product.

At present the production of oxygen is being developed on a very large scale by fractional distillation at sufficiently low cost so that it may be used profitably in industrial furnaces where air was used before, increasing their effectiveness considerably.

Hydrogen

Hydrogen is next on the list of important industrial gases. It is made entirely from the decomposition of water by several methods. The simplest method and the one that gives the purest hydrogen is by electrolysis, electricity being passed through the water, decomposing it into hydrogen and oxygen. Another method is to pass steam over hot iron, the iron removing the oxygen to form iron oxide, leaving the hydrogen as the product. Perhaps the most common process is the water-gas process, in which the steam is passed over hot carbon, forming hydrogen and carbon monoxide. When mixed with a proper illuminant, this com-

bination is used for illuminating gas in cities. Or the carbon monoxide may be oxidized with more water vapor to carbon dioxide, producing still more hydrogen.

Hydrogen is used in a number of important industrial processes. We are all familiar with Crisco and other lard substitutes. These greases are made by treating cottonseed oil with hydrogen in the presence of a catalyst, which is a substance that causes chemical reactions to proceed more rapidly. Large quantities of hydrogen are used in the oxyhydrogen torch or flame to obtain the high temperatures needed in the manufacture of artificial rubies and sapphires. Hydrogen is also needed to combine with nitrogen in one of the methods already mentioned for making ammonia. And we all know how hydrogen is used for balloons and dirigibles, although its inflammability makes it a dangerous servant when used for this purpose. The United States makes over 300 million cubic feet of hydrogen per year, not including that made and sold in the form of illuminating gas.

Helium

Another gas that is often associated with hydrogen in the public mind is helium, which is used in airships to take the place of hydrogen, it being noninflammable and having almost the same lifting power. The only reason that it is not used exclusively is on account of its scarcity, it being one of our rarest gases. It is present in the sun in large quantities, but that is a little too far off to be of much use to us. It is also given off when radium decomposes. But with radium worth thousands of dollars a pound, we cannot count on that source, so it is necessary to go to certain natural gases in our Southwest where helium has been

found to occur to the amount of around 0.5 per cent, still a small quantity. But by treating very large quantities of the natural gas by liquefaction and distillation, it has been found possible to produce quite pure helium at a cost about one hundred times that of producing hydrogen. During the World War we produced something like 200,000 cubic feet of this interesting gas. The United States Government has recently placed some of these natural gas wells under lock and key to insure a supply of helium for our airships in case of a national emergency.

Natural Gas

A gas of the greatest importance and which is given to us by nature is natural gas. This is obtained from wells or rather small holes driven deep into the earth, sometimes in localities where petroleum is found and sometimes where none is present. It is composed chiefly of hydrocarbons, that is, gases which consist of combinations of carbon and hydrogen united into various chemical combinations. The chief of these hydrocarbons is methane, a gas containing about 25 per cent hydrogen and 75 per cent carbon. Natural gas also often contains considerable amounts of gasoline of such a quality that it is used to enrich the low-grade gasolines produced elsewhere and make them fit for use in automobile engines. Natural gas is chiefly used for heating in place of artificial illuminating gas, and is often pumped for hundreds of miles through pipe lines to cities where it is consumed. Another large use for natural gas is in the manufacture of carbon black or gas black, one of the pigments used in the manufacture of black paint, but more especially in the manufacture of rubber tires for automobiles.

One of the reasons why modern tires give greater mileage than tires used to give is the improved quality obtained by using gas black in their manufacture. Unfortunately the process used in making gas black from natural gas is very wasteful of the gas and many States have forbidden its use for that purpose. In 1918 the United States produced over 700 billion cubic feet of natural gas, valued at over one hundred and fifty-three million dollars.

There are a number of other hydrocarbon gases of great industrial importance, such as ethylene and propylene, products of the heating of organic materials like soft coal and petroleum, which may be converted into valuable chemicals such as solvents and dyestuffs. The chemical industry is making greater and greater use of such processes and there may be a wonderful development in this field in the future.

Acetylene

Another hydrocarbon of the greatest importance is acetylene. This gas is made by putting water on calcium carbide, a product of the electric furnace, and it is used in a variety of ways. Its greatest use is in the oxyacetylene cutting and welding torch, with which wonders have been done in the welding together of metals and in the cutting up of old machinery and ships, sometimes many feet under the sea. Acetylene is compressed in strong steel cylinders to be shipped from the plant where it is made to the point of consumption. An interesting thing in connection with this is that when compressed by itself acetylene is very explosive and there have been some disastrous explosions from it. But if the gas is dissolved under pressure in a liquid called acetone, it is not explosive and

may be handled with perfect safety. This is the way it is compressed in the well-known Prest-o-Lite cylinders, which were used so much on automobiles before electric lights were common.

Carbon Dioxide

Carbon dioxide, or carbonic acid gas, is another gaseous compound of carbon, this time with oxygen. No doubt in Revolutionary days it was called dephlogisticated carbon because it is made from carbon by burning it in the air or in oxygen. Nowadays it is made from the flue gases given off when coal is burned, by scrubbing the gas with a solution in which the carbon dioxide is soluble, and boiling the gas out of the solution afterwards. It is then compressed into cylinders under a pressure of a thousand pounds per square inch, and shipped to soda fountains where it is used to carbonate the beverages. The little bubbles that rise in a glass of ginger ale are carbon dioxide bubbles escaping into the air. In 1919 the United States used nearly sixty million pounds of this gas in its soft drinks. Carbon dioxide is also used in making our washing and our baking soda, but its source is not from furnace gases but from the burning of limestone to make quicklime, the gas being evolved in the burning process. The soda industry requires a great deal of this gas, amounting in this country to something over half a million tons a year.

Chlorine

A gas of great industrial importance which received much unpleasant notoriety during the World War is chlorine, one of the constituents of our common table

salt. When in the free state—not in combination with some vigorous restraining substance like sodium—it is a very poisonous, irritating yellowish gas, and a good thing from which to keep away, but in the combined condition our modern civilization could not very well get along without it. It is used in making bleaching powder, chloroform, all sorts of important chemicals, the new antiseptic, Zonite, that is advertised so much, and is made by passing an electric current through a solution of common salt, a large amount of it going into the manufacture of liquid chlorine.

Chlorine is made by passing electricity through salt solution in a special kind of apparatus where the chlorine is evolved and caustic soda is also produced. The gas is purified and compressed into strong steel cylinders for shipment. It is used very extensively for the purification of municipal water supplies, killing all the harmful bacteria in the water. It is such a powerful poison that it is possible to make the water completely sterile, free from typhoid and other dangerous germs, and yet leave it absolutely free from the well-known chlorine taste and perfectly harmless for human use.

The United States uses about half a million tons of chlorine per year sold as such. During the World War it was made on a much greater scale for use in the manufacture of poisonous gases. It is interesting to realize that chlorine is not only the basis for our most dangerous military gases, but is also the basis for our best antiseptic and disinfectant against disease, a really versatile substance.

There are many other gases of industrial importance, such as sulfur dioxide, the basis for the manufacture of sulfuric acid, probably our most important chemical, and carbon monoxide, one of the chief sub-

stances in water gas. But a complete list would occupy a great many pages and would prove monotonous reading. It is quite remarkable to think that all these gases and their properties have been studied and put to use for the benefit of mankind since the time when your great, great grandfather went to school and learned all about that imaginary element called phlogiston.

CHAPTER X

GLASS: ONE OF MAN'S BLESSINGS

ALEXANDER SILVERMAN

Head of the Department of Chemistry, University of Pittsburgh

Do you know the first industrial enterprise attempted within the present territory of the United States? It was glass manufacture. And do you know what the first shipload of manufactured goods exported from America contained? Again glass. The industry which annually produces over two hundred and fifty million dollars' worth of glass in this country had its American start about one mile from Jamestown, in the Colony of Virginia, in 1607. Captain John Smith tells the story in his fascinating "History of Virginia" and the subsequent history is interestingly told by F. W. Hunter in his book on "Stiegal Glass."

"But," you ask, "did glass-making have its origin in America?" No. Recorded history is too young to give a definite answer to its origin. Certainly this indispensable material of modern civilization had its crude beginning over three thousand years ago. The Bible tells us in Genesis, iv, 22, that Tubal-Cain (born 3870 B. C.), the eighth man after Adam, was proficient in the working of brass and iron. The use of fire and clay ovens was known, and slags, or glassy substances, necessarily formed. The book of Job, xxviii, 17, philosophizing on "Wisdom," reads, "She cannot be estimated after gold and glass." Solomon's proverbs

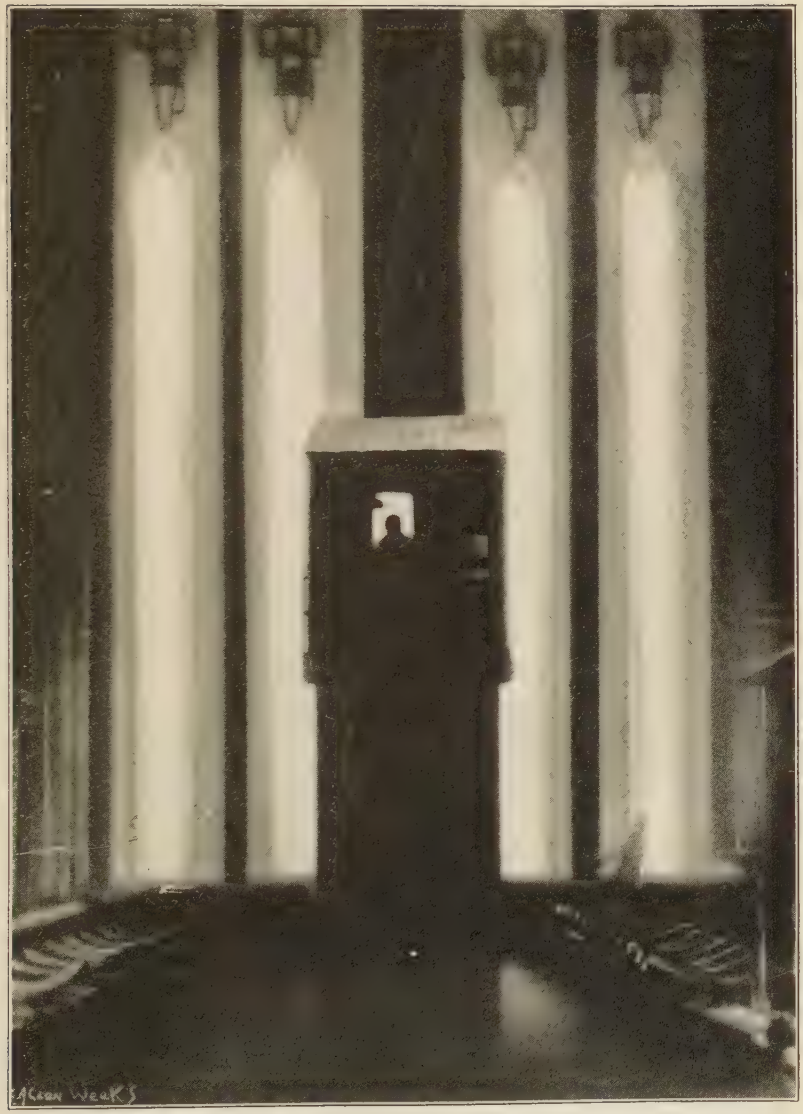
also mention glass. Pliny credits the discovery to stranded Phœnician sailors who landed on the shores of the Belus River in Syria. It was customary in those ancient days to rest kettles on large stones when cooking a meal. There were no stones on the shore, so the sailors tried lumps of natron from their ship and found to their amazement that the wood ashes, natron, and sand melted together under the heat of the fire and formed glass. So you see we do not know when or where glass was first made. We do know that the industry flourished in Egypt in 1500 B. C. Glass was precious in ancient times, some nations demanding tribute in this fragile material instead of gold. That the industry and its secrets were carried from country to country is further evidence of its intrinsic value. Victorious armies took the art from Egypt to Phœnicia, from Phœnicia to Greece, from Greece to Rome, from Rome to Constantinople, thence to Venice and the countries of western Europe, and finally the Great War established American supremacy in glass manufacture. M. A. Wallace-Dunlop relates its history in the Eastern Hemisphere in "Glass in the Old World."

But why speak of glass? What has this to do with you and me? Much. Glass is an important factor in civilization. A moment's reflection will help us to realize our dependence on glass. We should have no knowledge of the worlds of space or the realm of very small things like bacteria without the telescope or the microscope. In war and peace we should be without the periscope, field glass, the surveyor's instruments, range finder, and X-ray apparatus. The mariner's compass and our time pieces would be uncovered and lose accuracy. Our eyesight would suffer from lack of correction. We should be exposed to the elements

in inclement weather. Factories would cease operating during such periods and the display of the shop window would be no more. We should have no radio and night would find us in darkness for lack of the electric bulb and lamp chimney unless we returned to the candle or tallow-dip. Many household utensils would be missing and we should be without bottles for medicine, milk, and other beverages. These are but a few of the things that would happen. Fortunately the mirror would not be here to reflect our sorrow.

How Glass is Made

But we have glass and plenty of it. Now how is it made? You can make common glass (soda-lime glass) yourself. Thoroughly mix 100 grams of white sand (largely silica), 35 grams of soda ash (dried washing soda, the chemist calls it sodium carbonate), and 15 grams of limestone (principally calcium carbonate). Place this mixture (the glass-maker calls it batch) in a cup or crucible made of fire brick (the light gray material used for building) and heat it in a stove or furnace at or above 1260° Centigrade (2300° Fahrenheit) until it melts to a clear mass about as stiff as ordinary molasses on a warm day. During the melt the limestone and soda ash lose carbon dioxide, which comes off as a gas. Consequently, the glass will be full of bubbles if not heated long enough. If you will next dip the end of a narrow iron pipe into the glass and gather a small ball, you can blow it into a bulb or hollow object of any desired form. If you have some one attach the heated end of an iron rod to the bulb, opposite the blow-pipe, and you walk away from your friend, you can draw a glass tube. By proceeding in



Courtesy, Pittsburgh Plate Glass Co.

Like Cathedral Columns.

Some manufacturing processes are grimy, but here is one that is undeniably beautiful. The drawing of window glass cylinders.

the same way with the soft ball before blowing into it, you get a glass rod. And by pouring some of the soft glass into an iron mold and forcing a plunger into it, you could make buttons, marbles, bowls, lighting shades, and what not. Of course you would need more glass for the larger objects.

The sort of glass just discussed is used for making bottles. The window-glass manufacturer introduces salt cake (sodium sulfate) to take the place of part of the soda ash. Are bottle and window glass made in crucibles like the one you used? Rarely, today. They are made in continuously operating rectangular tanks, melting ten to six hundred tons of glass per day. The raw materials and broken glass (cullet) are introduced from time to time at one end through an opening called the "dog house." About two-thirds of the length away from the dog house an arched wall extends from above part way into the glass, or fire-clay floats may lie on the surface. In the melting end of the tank the raw materials stay near the surface as the air spaces make them lighter than the molten glass. When the materials form glass, this sinks and passes under the arch or fire-clay floats, where it is gathered by hand or machine, as the case may require. In some factories it is pressed in molds into shapes and bowls or blown into bottles and jars; in others, it is ladled into shallow, open pots. A pipe is lowered into it which blows a bubble about 2 feet in diameter on the surface of the molten glass, and this is drawn up into a window glass cylinder about 40 feet long. The cylinder is then cracked off at the bottom, lowered onto a support, cut into shorter lengths by an electrically heated wire, and the short cylinders are slit into halves, lengthwise, by hot rods, after which they are placed in a flattening oven, concave side up, and heated and

flattened into sheets. This is the development of a process invented by J. H. Lubbers about 1896.

It has been the aim of inventors for over forty years to draw glass into a continuous sheet instead of splitting and flattening cylinders. This is now possible. The late Emile Fourcault, a Belgian, and Irving W. Colburn, an American, have devised processes which are in actual operation. Such experiments are exceedingly costly, but through the financial coöperation of the late Michael J. Owens, inventor of the wonderful bottle-blowing machine, the Colburn process is in operation. In this a bar is lowered into the glass, which adheres to it and cools and solidifies as the bar is raised, the thickness of glass depending on the rate at which it is raised. At a certain point higher up, the sheet bends over rolls and travels horizontally through an annealing oven, where it is cooled down slowly to remove strains and prevent breakage. It is then cut into smaller sheets and dipped into acid to remove the dull film on the surface. The annual product of our cylinder and sheet factories would be sufficient to cover a roadway over twelve feet wide encircling the earth.

Why all this talk about window glass? What has chemistry to do with it? Make some taffy and try different kinds of sugar. Try various temperatures and heat each lot a different length of time. When you pull these taffies you will notice that they do not work alike. Their stiffness, or viscosity, will not be the same. And so it is with glass, only we must be much more particular. The chemist analyzes the raw materials from which glass is made, changing the quantities used on this basis so that the proportion of the various materials is constant; in other words, the chemical composition of the glass is always uniform. The tem-

perature of the furnace must not change or the glass will become harder or softer, not drawing uniformly. Surely you would not wish to look through glass full of bumps and waves unless you visited some side show at the circus and anticipated seeing grotesque-looking creatures. If the chemist had not found that acid would remove the dull film from the surface, everything would seem blurred when we look through the window. Nor should we want to see the pane shatter with every strong gust of wind. The strengthening of glass by adding salt cake and alumina, the latter found in common clay, is the result of experiment or research. And so we could go on and on if space were available. You can learn more about window glass in a little book on "Flat Glass," by Arthur E. Fowle. Trade catalogues of various glass companies contain interesting information and "Glass Manufacture," by Walter Rosenbain, gives a good general idea of the entire glass industry.

Plate Glass

How is plate glass made? The raw materials are like those used in window glass, but most manufacturers melt them in cylindrical pots, open at the top, in a rectangular furnace. A flange at the top of the pot permits it to be lifted out of the furnace by large iron prongs, after which scum is scraped from the surface of the glass, and the clear residue is poured on a steel table provided with shallow projecting tracks near the edges, over which a large steel roller passes to flatten the glass into a sheet. The principle is like flattening dough with a rolling pin when mother makes her pie crust. In a few plants plate glass is rolled continu-

ously, being fed from a tank furnace. After the plate has formed it is ground to remove surface irregularities and then polished with rouge (finely divided iron rust). This perfectly flat surface insures an undistorted image of objects seen through the glass and makes plate superior to window glass. However, window glass manufacturers are making great efforts to produce a uniformly thick and even glass. This is a difficult problem.

By the way, it might be interesting at this point to mention reënforced glass. This is made by working wire screening between two layers of molten glass, or by fastening several layers of plate glass together with some plastic or gummy cement, under pressure. The latter has been christened "transparent steel" by one writer, since one can stand in perfect safety behind a plate an inch thick and let some one fire a .45 calibre steel-nosed bullet at the plate. A 2-inch plate will withstand a 30-30 machine gun bullet. This property makes bullet-proof glass valuable for transparent partitions in banks. Of course the primary purpose for which wired glass and the other variety are made, is to prevent the flying of glass and subsequent injury in automobile accidents. These glasses may crack but will not break and scatter.

Would you like to know how colored glass is made? If you will look through a piece of window or plate glass edgewise you will observe that it looks green. This color is due to iron which occurs as an impurity in the sand and limestone. Manganese dioxide, a black powder, if added to the other raw materials, removes the green color; so does selenium, another black powder. On the other hand, manganese dioxide in larger quantities produces an amethyst color and

selenium a red, so you see the chemist must know how much iron is in the sand and limestone, that he may add just enough corrective material.

Well, you wanted to know how color could be produced, but were told how it could be removed. Before taking up color production it might be well to devote a little more time to the colorless glasses.

Have you seen cut glass, with its beautiful play of color when the light strikes it at certain angles? Well, that is made by using litharge or red lead (lead rust corresponding to iron rust) instead of lime or limestone. Pearl ash (potassium carbonate) takes the place of soda ash, and as lead is easily converted into metal, niter (sodium nitrate) is added to prevent this. You have partly lowered a pencil into a glass of water and it looked bent, yet you knew that the pencil was straight. Light passes through water at a different angle than it does through air. That accounts for the distorted appearance of the pencil. This bending of rays of light the physicist calls refraction, and the amount of refraction in glass depends on what you use in making the glass. Red lead and pearl ash in cut glass so bend and break the light rays that the beautiful play of colors of the rainbow results.

Optical Glass

The study of effects of various chemicals in glass on the light passing through such glasses has given us a great variety of optical glasses for correcting vision, use in telescopes and microscopes, X-ray bulbs, and other devices. A chemist, Otto Schott, made many of these discoveries in Germany from 1880 to 1900. The United States Bureau of Standards and the Geo-

physical Laboratory of the Carnegie Institution of Washington, coöperating with our manufacturers of optical glass during and since the European war, have established American independence in this field. An oxide is the dried rust of a chemical element, just as iron oxide is the rust of iron. In addition to the substances already mentioned, the oxides of zinc, barium, aluminium, strontium, boron, and a number of other chemical elements produce colorless glass. The chemist tries to substitute these, partly or entirely, for the materials used in the first glass discussed in this article, to study their effect on light, toughness, expansion under heat, and other properties. Much still remains to be done. Some materials have not been tried. Others may produce more desirable results if we change the proportions. Such experimenting is called research. Research means progress, more comforts, a better civilization.

Glass in the Kitchen

At dinner last evening a steaming-hot pudding was brought to the table in a glass baking dish. How was that made? Otto Schott, who was mentioned in connection with optical glass, experimented on the effect of boracic acid (the kind you use in solution as an eye wash) in glass. He found that it not only introduced properties valuable in lenses but that glass containing it and less soda ash would not break readily if heated and chilled suddenly. Such a glass was needed in chemical laboratories where solutions which would attack metals had to be heated, and its use was for many years confined to this purpose. While laboratory glassware had been made in the United States

prior to the European war, it was not so good as that made by Schott. With the war came a glass developed by E. C. Sullivan at Corning, N. Y., which was even better than that of Schott, and ere long it was found that this, and similar American glasses, could be used for oven doors and as cooking ware in the home.

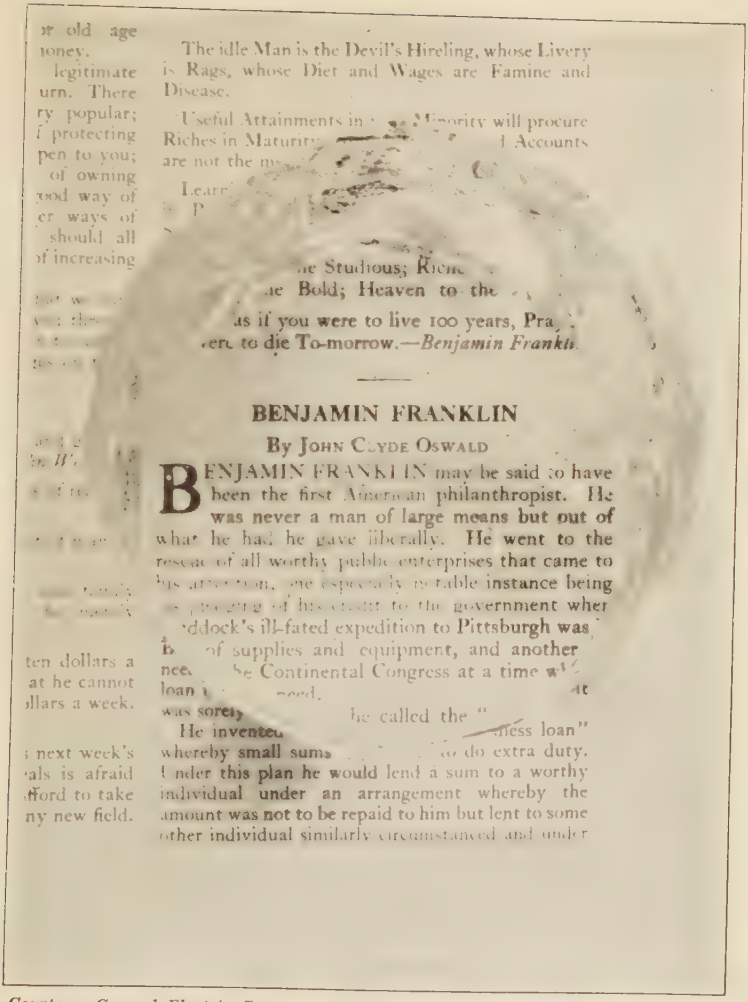
Yes, you are anxious to hear about colored glass, but cooking ware brings to mind another glass fact which we should not overlook. The space in your refrigerator between the enameled interior and wooden exterior may be filled with glass wool. If you heat the end of a glass rod you can draw the soft glass out to the diameter of the thinnest fiber. The glass threads are so fine that more than two thousand would have to lie side by side to fill an inch space and a ruler 1 foot long and 2 inches square (4 pounds of glass) can be drawn into a thread which will reach from New York to San Francisco. A mass of this material looks like a silky wool, so it is called glass wool. Many years ago, toy animals were made of it in France, hardly a good use, as the tiny glass splinters penetrate the skin and produce an annoying itch. Now it is used to keep hot things hot and cold things cold; in other words, as an insulating material. Glass wool is very light. This insulation used around the steam lines of a battleship instead of ordinary insulating material has been estimated to lighten the ship's load 380 tons, equivalent to the weight of forty-five hundred people, further requiring less draft and consequently effecting a saving of fuel.

Just a moment more and we will certainly discuss those colored glasses for which you have been waiting. But, why more delay? Well, have you ever visited a museum and seen an exquisite water-clear rock crys-

tal ball or carving? Rock crystal is very pure silica; in other words, a transparent material like sand or quartz but very pure. Edward R. Berry and his associates in the Thomson Laboratory of the General Electric Company at Lynn, Mass., recently melted small pieces of rock crystal in an electric furnace, controlling the pressure so as to remove all air bubbles, and produced what looked like glass. But it is different from glass. You can heat it red hot and plunge it into water without breaking it. It lets through all kinds of light, the heat and health-giving rays, even X-rays. You can get as good a sun bath through this glass as on the beach, and in midwinter. It is so transparent that you can clearly read this print through a block 25 centimeters (10 inches) thick. If you bend a rod of it into the shape of a letter "S" and push one end of the "S" into a hole in a closed box containing an electric light, you can see the light coming out at the other end of the "S". The light seems to travel around corners or in a circle. What the properties of this remarkably transparent fused quartz will mean to astronomy, microscopy, photography, the motion picture, lighting, medicine, and science generally can hardly be estimated at present.

Colored Glass

And now for the colored glasses. Let us consider them in the order of colors in the rainbow or spectrum; namely, red, orange, yellow, green, blue, and violet. The oldest red glasses were made with gold. If a solution of gold in acid (aqua regia) is poured over a small quantity of sand, the sand dried, added to the other materials used in making cut glass, and



The idle Man is the Devil's Hireling, whose Livery is Rags, whose Diet and Wages are Famine and Disease.

Useful Attainments in [illegible] Minority will procure Riches in Maturity [illegible] Accounts are not the m[illegible]

Learn[illegible]

[illegible] Studious; Rich[illegible]
[illegible] Bold; Heaven to the [illegible]
[illegible] as if you were to live 100 years, Pra[illegible]
[illegible] to die To-morrow.—*Benjamin Frankl[illegible]*

BENJAMIN FRANKLIN

By John Clyde Oswald

BENJAMIN FRANKLIN may be said to have been the first American philanthropist. He was never a man of large means but out of what he had he gave liberally. He went to the rescue of all worthy public enterprises that came to his attention, one especially notable instance being [illegible] of his credit to the government when [illegible]ddock's ill-fated expedition to Pittsburgh was [illegible] of supplies and equipment, and another nee[illegible] the Continental Congress at a time w[illegible] loan [illegible] need. [illegible] was sorely [illegible] he called the "[illegible]ness loan" He invented [illegible] whereby small sums [illegible] do extra duty. Under this plan he would lend a sum to a worthy individual under an arrangement whereby the amount was not to be repaid to him but lent to some other individual similarly circumstanced and under

Courtesy, General Electric Co.

A Printed Page Seen through a Slab of Transparent Fused Quartz Three Inches in Diameter and Nine Inches Long.

all are thoroughly mixed and melted, we get a yellow glass. When this is reheated in a smoky (reducing) flame and cooled again it is red. Reheated and cooled once more it becomes purple, and by repeating the treatment it may look blue when held up to the light. Why will gold produce all of these shades? When the glass was yellow, the gold was dissolved in glass just as sugar is dissolved in water, but on heating in the smoky flame, metallic gold separated in small particles which were suspended in the glass. These particles, if from six to sixty millionths of a millimeter $\left(\frac{3}{12{,}500{,}000} \text{ to } \frac{30}{12{,}500{,}000} \text{ of an inch}\right)$ in diameter, are referred to by the chemist as colloidal. The smaller particles so break up the light as to produce a red or ruby color; the larger ones a blue; and, of course, particles of intermediate size produce intermediate shades. Copper was next used to produce red glass. Copper scale (similar in appearance to the iron scale you see in a blacksmith or forge shop, except that it results from beating and hammering copper) or copper oxide, together with charcoal, is added to other raw materials of a lime or lead batch, but niter is left out. With the charcoal in and the niter out we get a light olive glass which, on reheating, turns red. If the charcoal is left out and niter introduced, the glass is a beautiful marine blue without reheating. Gold glasses are expensive and difficult to make, though very beautiful; copper glasses absorb too much light, in other words, do not serve well for signal lights or semaphores at great distances, as, for example, in railroad service.

Chemists are always on the lookout for new uses for chemicals, and so Pelouze, a Frenchman, conceived the idea of making ruby glass with selenium, a waste

product in the copper industry. It was already known that sulfur produced an ugly, brownish-red glass, and selenium is chemically much like sulfur in what it does. Whether its relationship to sulfur, or the fact that it was found with copper, which gave red glasses, led to the experiment we do not know. However, using a batch in which zinc oxide takes the place of limestone or lime, and to which some cadmium sulfide (a yellow substance sometimes used in paints), selenium, and charcoal are added, you get a glass which, on reheating, is a beautiful red. What is more, the glass is highly transparent, that is, absorbs very little light, and so the signal can be seen at great distances. Most of our automobile tail lights are now made of this glass.

Orange glass is also made with selenium. If you add it to a soda-lime batch instead of using a zinc-oxide batch, the color is orange and not red. A beautiful golden-yellow glass can be made by adding cadmium sulfide to a soda-lime batch. You can also get a canary-yellow glass with a silver compound, and a greenish-yellow with uranium oxide. However, most of the yellow or amber glass is made by adding sulfur and charcoal to a soda-lime batch. Salt cake and charcoal will also give amber.

Green results from iron, which is an impurity in sand and limestone, as we observed on looking at window glass edgewise. More iron will, of course, give a deeper shade, and when this is wanted iron rust (ferric oxide) is used. Chromium compounds (sodium bichromate is usually employed) produce a yellowish green color.

You already know that copper oxide, with niter, added to a lime or lead batch, yields a marine blue

glass. To get a dark blue, you add cobalt oxide or a preparation containing it; again, niter is used.

Purple or amethyst shades result when manganese dioxide (in the presence of niter) is added to a lime or lead batch. Four to eight ounces to a hundred pounds of sand should suffice. If you add too much, the glass is still purple but so dark that it looks black. The same will happen if you add too much cobalt oxide to your blue batch. That is how black glass is produced.

Perhaps you have studied chemistry and made borax beads in a loop of platinum wire. If so, you will have observed that many of the colors produced in glass by the various chemicals resemble those you obtained in the borax beads.

To produce intermediate shades of green, blue, and violet glasses, it is only necessary to mix the different oxides yielding these colors in various proportions. While any shade of green, blue, or purple can be obtained, the problem is much more difficult for reds, oranges, and yellows.

All the glasses referred to thus far are transparent except the black. You have seen opalescent, milky, or white shades made for lighting purposes. This color results when a fluoride (fluorspar or cryolite) and an aluminium-bearing compound (feldspar, china clay, or alumina) are mixed with a lime or lead batch containing niter. Hydrofluoric acid, which is made from fluorspar and sold in paraffin bottles because it would eat through ordinary bottles, etches glass. The glass is covered with warm beeswax or various mixtures of this with asphaltum, and a design is scratched through the wax. Result, the deep line decorations on your water glasses. By using the wax on paper and applying it as you did to transfer pictures when a child,

other decorations result, and by mixing the acid with other chemicals and immersing the objects, you can get any effect from a deep line-cut through a satin finish to the dull white surface you see on electric bulbs. Wax is not used when lamp bulbs are etched; only when you want a design. To remove the wax, simply place the etched object in hot water. The wax melts off and floats to the surface of the water.

Great progress seems to have been made and has been made in glass manufacture since those Phœnician sailors built a fire on the shores of the Belus River thousands of years ago. The inventive genius of the engineer enables the United States to turn out annually over three hundred million electric light bulbs; enough water tumblers and goblets to provide each citizen with a dozen; plate glass which would pave a boulevard from coast to coast, or furnish a windshield to encircle the globe; enough window glass to cover a 20-foot driveway around mother earth at the equator; and twenty-five million gross of bottles to nourish us, keep us cool, and alleviate or cure our suffering. The chemist took part in this development by devising methods for the manufacture of better and cheaper chemicals; for insuring uniform glass; for making superior glasses. To him, also are we indebted for the optical glasses and many of the colors.

What have we then? Comforts and conveniences of everyday life, so much a part of our very existence that we are hardly conscious of them. Signals, to warn us of danger. Colors, assembled by the magic hand of the artisan, which, on one hand, add to the gayety of life, and on the other, in the stained glass window of the church and cathedral, inspire awe, reverence, faith.

A Few Future Problems

Much remains to be done. The pots and tanks in which glass is made corrode too rapidly, especially for certain types of glass. The glass is not always good, and that means monetary loss. There are colors we want and do not have. Other colors might be improved. Economics can be effected by substituting new chemicals without lowering the quality. And glass still breaks. Perhaps you have read the life of Tiberius, a Roman Emperor. It is said that a citizen invented a method for making malleable glass and was invited to visit the Emperor. He brought a vase which was thrown to the ground but only dented. A hammer again rounded it into shape. In those days tribute was paid in glass, which was as precious as gold because it was fragile, and so Tiberius asked whether any other man knew the secret of manufacture. The artisan answered "No," whereupon the Emperor ordered him beheaded.

Fortunately, we do not live in an age of secrets. We want progress. The American Chemical Society, the American Ceramic Society, and the Society of Glass Technology of England, together with similar organizations in France, Germany, and other countries, publish journals which tell of the progress at short and regular intervals. Trade journals and advertising literature also inform us and the popular magazines contain stories. Let us therefore add some aqua ammonia to a solution of silver nitrate (with which the doctor paints your throat when you have an ulcer) until it becomes dark and continue adding ammonia until the solution almost clears again. We will next wet a piece of clean glass with formaldehyde (the disin-

fectant) solution and pour the other solution on the glass, or into a flat bottle, shaking it gently. A beautiful mirror results. Let us now smile into that mirror and have it reflect our gratitude for the blessings glass has given us.

CHAPTER XI

THE ELEMENTS OF IRON AND STEEL MANUFACTURE

A. E. White

Director, Department of Engineering Research, University of Michigan

Hesiod, the Greek poet, about 700 B. C., divided the early history of man into four periods. The first he called the Golden Age; the second, the Silver Age; the third, the Bronze Age; and the fourth, the age in which he then lived, the Iron Age. Because of this classical division some feel that methods for producing bronze, and possibly copper, were known earlier than were methods for producing iron. This belief is supported to some extent by the fact that bronze and copper relics antedating any known iron relics have been found. It is not at all improbable, however, that iron was produced as early as copper or bronze. Our failure to find iron relics that were produced as early as our copper and bronze relics, is probably due to the relatively rapid rate at which iron disintegrates. We know, however, that iron was made as early as 3000 B. C., because in 1837 Hill broke from a masonry joint, made about 3000 B. C., a portion of an iron tool. Iron plowshares were in common use at the time of Rameses II, 1292-1225 B. C.

The modern metallurgy of iron and steel is a very recent development. There were no outstanding developments in the manufacture of iron and steel from the

prehistoric days mentioned to about 1860. To be sure, the early methods of converting iron ore into a metal, by heating it with charcoal under reducing conditions, underwent modifications. The hearth height of the furnaces used for the smelting increased from a few inches to 24 feet. Likewise, the production of what we now speak of as wrought iron was, in the later days of the period, produced in a two-cycle operation rather than in a single-cycle operation. That is, in place of making wrought iron directly from the iron ore, the ore was first converted into a hard, metallic substance, which we now call cast iron. This was then remelted under such conditions as would make it malleable and weldable.

The so-called crucible process was brought out in 1784. This process may be considered by some as radically different from that used by the ancients in the production of their steels. A process giving a resultant similar metal, however, must have been used in the manufacture of the famous Damascus blades.

About 1859 Sir Henry Bessemer in Great Britain, and William Kelly in the United States, developed a process which we now call the Bessemer process. It was a process which lent itself to the production of large tonnages of steel, and because we were enabled thereby to obtain steel in large quantities at a low price it has had a profound effect upon our civilization. Without it our railroads, our ocean steamships, our skyscrapers, our street railway systems, in fact the entire fabric of our present-day civilization would not have been possible. It is because of the outstanding effect this invention has had upon our civilization that we can look to it as a milestone and as the dividing line between ancient and modern metallurgy. Since that date we have had the development of the open-hearth

process, which has resulted in a higher grade product than is possible by the Bessemer process and has outstripped it in the matter of tonnage.

As further milestones, we can turn to the development of high-speed steel in 1900 by Taylor and White. We can also mention the rapid increase in the use of special alloy steels since 1905. It is not possible to name any given year of outstanding importance in this latter connection. The development has been gradual, though decided. It has made possible our automobiles and has therefore been no mean factor in our present-day civilization.

Modern Requirements

Investigations today are leading toward the development of heat-resisting and corrosion-resisting steels. Corrosion is the great enemy of iron and steel. We have no definite figures as to the extent of its ravages, but some have stated that it destroys at least one billion dollars' worth of property annually. We now know of a number of different types of corrosion-resisting steels. They possess excellent physical properties and can be worked and fabricated into any shape that ordinary steel will take. The only reason that these steels are not used more universally is their cost. As soon as that is brought to a lower value, there will be a generally universal application for these steels.

Likewise, we are using metals today under increasingly higher temperatures. We need, therefore, metals which will maintain to the highest possible degree the properties they possess at atmospheric temperatures. Much study and thought is being devoted to this field. The development of these classes of steels is so grad-

ual that it can hardly be spoken of as constituting an epoch, though the production of steels with these characteristics will have a profound effect and influence upon our civilization.

The early days of the iron industry in this country were confined to the Atlantic Coast. Iron ore was available in New York and in New Jersey and small pockets of it were found in many of the other States. The countryside was thick with standing timber. It was but a simple process to convert the wood into charcoal. Limestone, the other necessary ingredient, was also available. No difficulty, therefore, was experienced in getting such iron as was necessary for the early needs of this country.

Ore Resources

Today the Lake Superior region adjacent to Marquette, Michigan, and Duluth, Minnesota, supplies over 85 per cent of the iron ore used in the United States. Ore on the Marquette range was discovered on September 19, 1844, by William A. Burt. The first shipment of ore in any quantity consisted of 152 tons. This was in September, 1853. Since that date an ever increasing quantity of iron ore has been shipped to the smelting centers. The vessels used have changed from small-tonnage, wooden sailing vessels to giant ore carriers capable of transporting over 12,000 tons of ore. The use of vessels of this latter size has been made possible by government aid in the dredging of needed channels and especially by the installation of mammoth locks at Sault Ste. Marie. Modern methods of loading and unloading have been developed, so that 12,000 tons of ore can be loaded into a steamer inside

of 20 minutes. It does not take over 4 hours to unload this vast quantity of ore.

It is of an extremely high grade, consisting of about 56 per cent of iron, 24 per cent of oxygen combined with the iron, and 20 per cent of other substances, the main portions of which are water and silica. The ore from northern Michigan is for the most part harder and more compact than the ore from the great deposits on the Mesabi range near Duluth. The ore is brought from the loading docks at Duluth, Two Harbors, Marquette, or Escanaba, by boat to the smelting centers near Chicago and Cleveland. To these smelting centers is brought either coal, which has to be coked, or coke. Limestone is also shipped to these same centers from suitable locations not far distant from the centers themselves. Ore, coke, and limestone in the proportions of two tons of ore to one of coke and one-quarter of a ton of limestone, are fed into mammoth cylindrical furnaces 100 feet high and having a maximum diameter of 20 to 25 feet. Huge blowing engines provide the air necessary for the combustion of the coke, and large stoves adjacent to the furnace, each 100 feet in height and about 20 feet in diameter, provide the means for preheating the air so that higher temperatures are obtainable in the furnace than would be through the use of unheated air. A single furnace will consume, during the course of 24 hours, 1200 tons of air. It will produce 600 tons of pig iron, 400 to 500 tons of slag, and 1400 tons of waste gases. This pig iron contains, in the main, about 93 per cent of iron, 4 per cent of carbon, from 0.5 to 1 per cent of manganese, from 0.4 to 4 per cent of silicon, under 0.1 per cent of sulfur, and under 0.1 per cent of phosphorus. It is the base from which all of our iron and steel products of commerce are made; namely, our gray and

malleable iron castings, our steel castings, and our Bessemer, open-hearth, and electric-furnace steel products.

Some Kinds of Iron and Steel

Gray iron castings are essentially castings made from remelted pig iron. Slight variations in the silicon and carbon contents are effected in order to produce the desired qualities in the castings, the chief one of which is machinability. Gray iron as such under any condition is extremely weak and should not be used where strength or ductility is of prime importance.

Malleable iron is a remelted pig iron subjected to a heat treatment so that all of the resultant carbon is more or less uniformly distributed throughout the metal in the form of rosettes. This gives to the iron good machinability, fair strength, and fair ductility, although these last two properties are inferior to what can be obtained in steel.

The Bessemer steel process consists in blowing air through molten pig iron. In the acid Bessemer process, the only one of the Bessemer processes used in this country, the blowing of the air through the molten pig iron eliminates the carbon, the manganese, and the silicon. The blowing operation continues until these elements are completely removed. The resultant molten product is then treated with a substance known as ferromanganese, which gives to it the desired proportions of carbon, manganese, and silicon. These range from a mere trace to about 1 per cent for carbon, from 0.3 to 1 per cent for manganese, and from 0.05 to about 0.3 per cent for silicon, with most of the remainder iron.

The molten product with one of the foregoing compositions is then cast into ingots. These are masses of metal of different sizes. Some of the more common sizes are 60 inches long, and 18 by 22 inches in cross section. After the molten metal has been cast into these ingots it is allowed to cool to such a temperature that the outside of the ingot mass at least is firm and solid. The ingot proper is then placed in a soaking pit to heat it so that the entire section of the ingot will be of uniform temperature. It is removed from the soaking pit at a temperature of about 2000° to 2300° Fahrenheit and rolled into the shapes with which we are daily familiar; that is, it is rolled into rails, structural steel, steel plates, and other shapes. Sometimes the rolling operation is so conducted that no reheating is necessary after the metal leaves the soaking pit. Often, however, it is necessary to reheat it between the different forming operations, as metal when white hot is much more readily and easily shaped than metal at atmospheric temperature.

The open-hearth process was first suggested about 1866. It consists in melting large quantities of metal, usually pig and scrap, sometimes as much as 100 tons, in a large but shallow furnace. Sometimes in place of melting the metal, the hearth is filled with molten metal brought to it from the blast furnace or from some auxiliary melting equipment. The purpose of this process is to reduce the carbon, manganese, and silicon contents in the pig iron to such a point that the final product will be steel. This is the operation which is done in the acid open-hearth process. In the basic open-hearth process the sulfur and phosphorus are also reduced to the extent desired by engineers. The elimination of the carbon, manganese, and silicon is

effected by oxygen contained in iron ore. That is, iron ore is shoveled into the molten metal, and as the affinity of oxygen is greater for silicon, manganese, and carbon than it is for iron, the result is that the carbon, manganese, and silicon in the metal are oxidized as much as desired for the given operation. In the presence of a slag which is basic, namely a slag which is high in lime, sulfur and phosphorus are also oxidized and by that means eliminated to the extent required. After the oxidation process is completed, the metal is in turn treated with suitable reagents to give it the desired carbon, manganese, and silicon contents. It may seem paradoxical to state that these elements are first removed and then special efforts are taken again to introduce them into the metal. In rare instances, in some special applications of these processes, these elements are not completely removed in the oxidizing operation. The reason for the complete removal is that it is easier to produce the desired percentages of carbon, manganese, and silicon in a product completely free from these elements than in a product carrying slight quantities of them. Also, in the oxidizing process some of the iron is at times oxidized. Oxidized iron in steel is one of the most harmful substances. The introduction of proper quantities of silicon and manganese completely removes any oxidized iron. This is a further reason for the addition of silicon and manganese. Carbon, of course, is added for its own sake as its presence has a profound influence upon the properties of the steel. The resultant composition of the steel is very similar to that given for the Bessemer steel. Open-hearth steel is, however, for the most part lower in both sulfur and phosphorus. These elements are especially injurious in steel, the former bringing about great difficulty in

the formation of the steel, and the latter making the steel exceedingly brittle under shock.

These steels are shaped in the same manner as Bessemer steels, and their uses are similar to those for Bessemer steel. Open-hearth steel is rapidly replacing Bessemer steel, however, because it is a more uniform product and it is usually lower in sulfur and phosphorus content. It is but little, if any, higher in base price.

Wrought iron is a pig iron which has been refined in a so-called puddling furnace. The furnace is hearth-shaped. It only holds about 500 pounds of metal per charge. In the early stages of the refining operation the metal is liquid. Iron oxide, which is added to the molten metal, however, serves to reduce the carbon, manganese, and silicon contents. As the carbon is reduced in quantity the melting point of the iron is raised. Finally, the carbon is reduced to such a point that the iron becomes pasty. It is then removed from the furnace, although contaminated with slag. A large amount of this slag is removed during the forming operations, though about 2 per cent remains in the final product. It is an iron for which corrosion-resisting claims are made. Its sale is largely in such fields as require a corrosion-resisting metal.

The crucible process is essentially a melting process. Practically no purification is accomplished. Therefore, no undesirable elements must be in the charge. It is a process used for the production of tool steels.

The electric-furnace process is conducted in a manner very similar to the open-hearth process. The essential difference between the open-hearth process and that of the electric furnace is in the method of generating the heat. In the open-hearth process the

heat is generated through the combustion of gas or oil. In the electric-furnace process the heat is produced from electricity. This method is rapidly replacing the crucible process for the production of tool steel and is making heavy inroads in the alloy steel field. Doubtless, as time goes on, it will replace the open-hearth process, as the open-hearth process is today replacing the Bessemer process.

CHAPTER XII

THE MAKING OF LEATHER

JOHN ARTHUR WILSON

Chief Chemist, A. F. Gallun & Sons Company

A detailed study of the changes taking place in animal skin during its conversion into leather is made doubly fascinating by the possibilities which it presents for preserving one's health and beauty through a better knowledge of the skin and its functions.

THE SKIN

A fair idea of the structure of the type of skin used for leather manufacture can be gained by studying Figure 1, page 164, which is a photograph of a cross section of cowhide highly magnified. A slice of the hide, from the part known as the butt, was cut 0.02 millimeter in thickness by means of a microtome. It was mounted on a glass slide, suitably stained to show details, covered with Canada balsam, and sealed with a cover glass. The slide was then set in a microscope, through which the photograph was taken. The top of the picture shows the outer, or hair side, and the bottom the flesh side of the hide.

Most of the solid matter of such a hide consists of proteins, a very complex group of chemical substances made up of carbon, hydrogen, oxygen, and nitrogen. The skin also contains oily substances, blood, and inorganic salts.

The Epidermis

The skin is divided rather sharply into two parts differing both in origin and structure: the derma, or true skin, which forms by far the greater portion of the whole, and the epidermal system, comprising the epidermis, hair, and glands. The epidermal system, derived from the ectoderm or outer layer of the embryo, consists entirely of reproducing cells which rest on the surface of the derma and draw their nourishment from it. In the picture, the epidermis appears as a thin, wavy line bounding the upper surface and of a thickness only one two-hundredth of that of the derma below it.

The portion of the epidermis in contact with the derma is a layer of living cells, rather elongated in shape. It should be mentioned that a cell consists of a nucleus suspended in protoplasm enclosed between very thin walls acting as a semipermeable membrane. Nourishment from the blood diffuses through the cell walls and, after a certain period of growth, the cell divides mitotically, forming two cells. In the deepest layer of the epidermis each cell increases in height and then subdivides, forming two cells, one above the other. This process is repeated indefinitely. As the older cells are pushed outward, they become flattened by dehydration and other changes. During this process the protoplasm dries up and the cells lose their power of reproductiou. In the outermost layer the cells are dry and scaly and are gradually worn away. This scaling is often very noticeable on the scalp in the form of dandruff, which in itself is not the result of a disease, but rather is evidence that the epidermal cells are functioning and reproducing vigorously.

The Hair

To the naked eye the hairs appear to pierce the skin, but actually they do not do so. The epidermis dips down into the derma here and there, forming follicles, or pockets, in which the hairs grow. At the bottom of each follicle there is a projection from the derma known as a hair papilla, which is supplied with both nerves and blood vessels. Lining the space around the papilla are numerous epidermal cells, which derive from the blood the nourishment necessary for their reproduction. As new cells are formed, the older ones are pushed outward. In uniting to form the hair they assume the shape of the follicle; if this happens to be curved, the hair will be curly. Here we have the secret of curly hair; straight hair indicates straight follicles. To give a natural curl to such hair it is necessary to tease the follicles into a curved shape.

The rate of growth of the hair depends upon the supply of nourishment available for the reproducing cells surrounding the papilla. Baldness results from the failure of the blood vessels of the papilla to furnish the required nourishment or from the destruction of the epidermal cells in some other way. The great majority of cases of baldness would never have occurred had the victims, by massage or otherwise, kept the blood flowing through the scalp at a normal rate.

The blood also furnishes a pigment, containing iron and sulfur, which gives the hair cells their color. With lowered blood pressure in the scalp, the cells no longer receive this pigment and assume a gray appearance. The writer has observed that the first hairs to turn gray are those which happen to be closely crowded by other more vigorous hairs and he has apparently

succeeded in producing thin bands of color in such hairs by intermittent massaging.

The Derma

Unlike the epidermis, the derma, which is derived from the mesoderm or middle layer of the embryo, is not made up chiefly of cells, but of fibers which are produced by the activity of migratory cells very much smaller in size than the extracellular material which they produce. These cells become less numerous in the skin with increasing age of the animal. The fibers of the derma are of two kinds: the large, white fibers of collagen which make up the great bulk of the derma; and the thin, yellow fibers of elastin which occur only in the region of the upper and lower surfaces of the derma. In some types of skin, fat cells replace some of the collagen fibers. However, the greater the proportion of fat cells to collagen, the less valuable is the skin for leather making, since the collagen is the leather-forming part of the skin. The derma is also traversed by complex systems of nerves and blood vessels.

The Thermostat Layer

It will readily be noticed by glancing at Figure 1, page 164, that the derma divides itself rather sharply into two layers, the dividing line occurring at the lower extremities of the hair roots, or about one-fifth of the distance from the upper surface to the flesh. The lower, fibrous region of the skin is often referred to as the reticular layer because of the network appearance of the collagen fibers. The upper layer has been called by the writer the "thermostat layer" for a reason that will be made clear presently.

The advantage of dealing separately with these two layers will be appreciated when it is pointed out that the structure of the reticular layer determines the physical properties of the leather, such as tensile strength, solidity, resilience, etc., while the thermostat layer determines more particularly the appearance of the leather. In making the finer grades of leather, a great deal of attention must be paid to the thermostat layer. It is a matter of no small importance that this layer is almost as thick in the skins of very small animals as in those of very large ones; in the thinner skins, and even in the thinner parts of the same skin, this layer occupies a greater proportion of the total thickness. It seems as though a minimum thickness of this layer is required for its very delicate and complex operation.

In order to show the mechanism of the thermostat layer more clearly, the region around the third follicle from the left in Figure 1 was photographed at higher magnification and is shown in Figure 2, page 164. At this greater magnification it will be seen that the epidermis is divided into two layers: an inner layer of living cells, known as the Malpighian layer; and an outer, scaly layer, known as the corneous layer.

Attached to the base of the hair follicle and weaving its way upward to the right is the erector pili muscle, one being attached to each hair. Just above this muscle and emptying into the hair follicle is a cluster of sebaceous, or oil glands. The empty space near the lower left-hand corner is that formerly occupied by a sudoriferous or sweat gland. The muscle and glands make up what is essentially a most remarkable thermostat, which tends to keep the temperature of the whole body constant.

The muscles are controlled by pilo-motor nerves,

which are sensitive to temperature changes. If the surface of the skin is cooled, the muscle is made to contract. The effect to the naked eye is the phenomenon commonly known as gooseflesh. The contraction of the muscles puts a pressure on the sebaceous glands, causing the cells to give up their oil to the hair follicle, through which it flows to the surface of the skin. In this operation the flow of water from the sweat glands to the surface of the skin is stopped or retarded, thus preventing loss of heat through the evaporation of water. Enough of the heat generated by the body is thus conserved to keep the body temperature constant.

When the body is subjected to high temperatures, the muscles relax, tending to draw in any free oil and at the same time opening wide the ducts of the sweat glands, allowing a free flow of perspiration, the evaporation of which consumes all heat in excess of that required to keep the temperature of the body constant. When the skin is subjected to a very sudden drop in temperature, especially from a relatively high temperature, the thermostat layer seems to become temporarily paralyzed and the work of throwing off water is added to that already carried by the lungs. The result is a cold or an even more serious disease.

The erector pili muscles also contract under the influence of emotions such as fear, surprise, anger, or other disagreeable states. The visible effect is sometimes that of the hair standing on end, as in a frightened cat. The oil secreted by the sebaceous glands, in contact with air, thickens to the consistency of ear wax, to which it is related. When the ducts become clogged with dirt, the pressure behind them causes them to become distended, giving rise to blackheads or pimples.

Tannery Operations

The description of tannery operations will be limited to a brief survey of a specific series of operations in actual use for making shoe upper leather, but the basic principles governing these operations apply generally to the manufacture of nearly all kinds of leather. In making the leather described, calfskins are used.

CURING

Although the inner surface of the skin on the living animal may be free from bacteria, it acquires them rapidly from the air from the instant of flaying and acts as an ideal medium for their reproduction, which takes place at the expense of the leather-forming proteins of the skin. In order to guard against damage by bacteria, it is customary to apply dry sodium chloride to the skins until the solution retained by the skin is nearly saturated with salt. The application of salt lowers the water content of the skin from about 65 to 45 per cent.

As long as the solution wetting the skin contains more than 6 per cent of salt, there is little danger of putrefaction at low temperature. On the other hand, if the strength of the salt solution falls below 1 per cent, the bacteria may be more active than if no salt had been used. As an added safeguard, the salted skins are kept in a refrigerator until wanted. The process of salting is generally known as curing.

SOAKING AND FLESHING

The first tannery operation is that of soaking in vats of water in order to cleanse the skin and to restore

the water lost through partial drying. As soon as the skin has absorbed enough water to restore its natural size and shape, it is fleshed. In this operation, the flesh side of the skin is forced against a revolving roller set with sharp blades, which cut away the adipose tissue. Figure 3, page 164, shows a cross section of a fresh calfskin. The bottom quarter of the picture is occupied by the adipose tissue, which connects the skin loosely to the rest of the body. This consists chiefly of fat cells and loose strands of connective tissue, and has practically no value in leather making. Together with trimmings, it is used in the manufacture of gelatin.

After fleshing, the skin is soaked again until freed from most of the soluble protein matter normally present in the blood vessels and lymph spaces. The skins are usually given a change of fresh, cold water each day for three days.

Bacterial counts are made of the soak water in order to guard against any dangerous increase in numbers, which would require the use of a disinfectant to protect the skins against damage.

LIMING

The cleansed skins are next put into a vat, equipped with a paddle wheel to keep the liquor well stirred, and treated with limewater containing a small quantity of sodium sulfide. Lime in excess of that required to make a saturated solution is used so that the liquor remains saturated at all times. This liquor slowly destroys the Malpighian layer of the epidermis, effecting a practically complete separation of the entire epidermal system from the true skin.

Figure 4, page 164, shows a cross section of calfskin

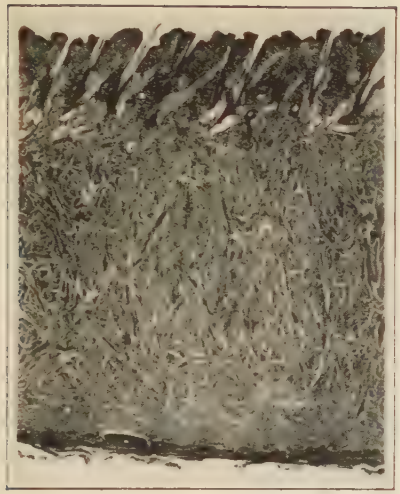


Fig. 1.—Vertical Section of Cowhide, Magnified 16 Diameters.

Fig. 2.—Thermostat Layer of Cowhide, Magnified 75 Diameters.

Fig. 3.—Vertical Section of Calfskin (Fresh), Magnified 30 Diameters.

Courtesy, A. F. Gallun and Sons Co.

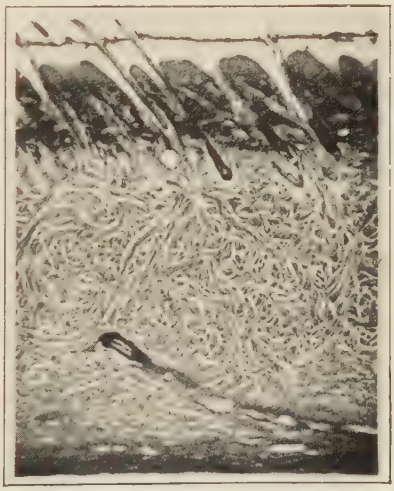


Fig. 4.—Vertical Section of Calfskin (after 48 Hours in Lime Liquor), Magnified 35 Diameters.

which has been in a lime liquor for two days. It will be noted that the hairs and glands are entirely separated from the skin and that the corneous layer of the epidermis forms a thin sheet quite removed from the derma; it appears in the picture as a horizontal line just above the true skin.

In Figure 4 a large vein can be seen running downward to the right from a point in the main body of the skin. In Figure 3, page 164, at the middle of the lower part of the reticular layer, is a cross section of one of the trunk-line arteries which supply the skin with nourishment. A knowledge of the structure of the blood-vessel system of a skin is of great importance in the manufacture of fine grades of shoe upper leather.

UNHAIRING AND SCUDDING

From the lime liquor the skin is transferred to an unhairing machine in which the hair side of the skin is forced against a revolving roller set with blades which scrape off the loose hair and epidermis. The skin is then thrown over a convex, wooden slab, called a beam, and a man pushes a specially designed, two-handled knife downward over the skin and to the left and right, forcing out the loose material from the hair follicles and pores. The operation is known as scudding and the operator as a beamster. After scudding, the skins are washed with running water in an open, revolving drum in order to remove the free lime. Figure 5, page 168, shows a cross section of calf-skin which has been limed, unhaired, scudded, and washed. It is now practically free from the various parts of the epidermal system and is ready to be bated.

BATING

The skins are next transferred to a paddle vat containing a very dilute solution of pancreatic enzymes and a salt which neutralizes the caustic alkalinity of the skins. The lime causes the skins to swell up and become rubbery, but the bate liquor counteracts this effect and the skins quickly lose their resilience and become flaccid. At the same time the enzymes act upon the elastin fibers of the skin, dissolving them to a greater or lesser degree, depending upon the amount of enzyme used and the time and temperature of the digestion.

Figure 6, page 168, shows a section of calfskin taken after bating, in which all of the elastin fibers have been dissolved. This action can be seen very clearly by comparing Figures 5 and 6, page 168, which show the same skin before and after bating. In Figure 5 the elastin fibers appear as dark threads in the upper and lower layers but not in the middle portion of the skin; in Figure 6 they are not to be found anywhere.

The elastin fibers tend to prevent an extension of the surfaces of the skin; their removal makes the grain surface of the skin more readily extensible, which is sometimes, but not always, advantageous. The extent to which the bate liquor is permitted to dissolve elastin is governed by the specific properties wanted in the leather.

Besides rendering the skin flaccid and removing some of the elastin, the bating operation has a third purpose, which is to cleanse the skin, freeing it from any scud and partially decomposed proteins not previously removed. Two or three decades ago, bating was done almost entirely with warm infusions of the

dung of dogs or fowls. It was then a most disgusting and disagreeable process. Happily, the use of materials of this sort has been abandoned wherever scientific methods are employed.

The bated skin shown in Figure 6 is composed almost entirely of fibers of the protein collagen and it is now ready to be tanned. Up to this point the operations have been conducted chiefly with the object of removing constituents of the skin not wanted in the leather. In practice, the collagen fibers almost invariably suffer some damage during the removal of the undesirable parts of the skin. Any lessening of this damage is of great money value to the tanner and the possibilities for improvement in this direction are still so great as to make this a tempting field for chemical investigation.

Vegetable Tanning

Two very different methods are employed generally for converting the raw skin into leather: vegetable tanning, which is of ancient origin; and chrome tanning, which has been in general use only for about thirty years. Bated skin is highly putrescible, but when brought into contact with those materials which are known as tanning agents, it assumes new properties, one of which is resistance to putrefaction. In vegetable tanning the bated skin is suspended from a stick, head down, into a vat containing a weak infusion of barks, woods, and leaves containing tannin. The first liquor into which the skin is put is the weakest and one which has been used many times before. Each day it is transferred to a stronger and fresher liquor until fully tanned, which takes about ten days.

During the time the skins are in the tan liquors,

the tannin slowly diffuses into the interior of the skin and then into the very substance of each fiber. The collagen and tannin then combine to form a new material, leather, which is neither collagen nor tannin, but a quite different substance having the properties of neither of the constituents which combined to make it. When the tanning is complete, each collagen-tannin fiber appears under the microscope like a transparent rod of brown glass. In actual practice about sixty parts of tannin combine with one hundred parts of collagen.

Chrome Tanning

In the newer method of tanning, the bated skins are first pickled in a bath of sulfuric acid and sodium chloride and then treated with a solution of basic chromium sulfate, having the chemical formula $CrOHSO_4$. The chrome liquor diffuses rapidly into the skin substance and a combination takes place between the collagen and chromium, forming the substance known as chrome leather. When collagen is brought into contact with boiling water, it is rapidly converted into gelatin and as such passes into solution. Chrome leather, on the other hand, remains unaffected by boiling water. A test frequently used in the tannery to determine when a skin is fully chrome-tanned is to keep it in boiling water for five minutes. If it has not curled up at the end of this time, it is considered tanned. Of course the combination of chromium with collagen is not always stopped at this point; for some kinds of leather it is desirable to carry the tanning further.

The protein also combines with sulfuric acid during the operation, free acid always being present in solu-

Fig. 5.—Vertical Section of Calfskin (before Bating), Magnified 35 Diameters.

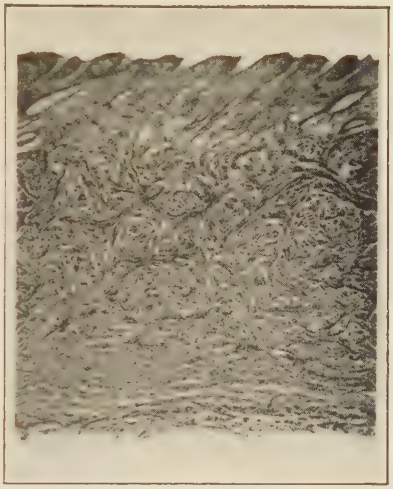


Fig. 6.—Vertical Section of Calfskin (after Bating), Magnified 35 Diameters.

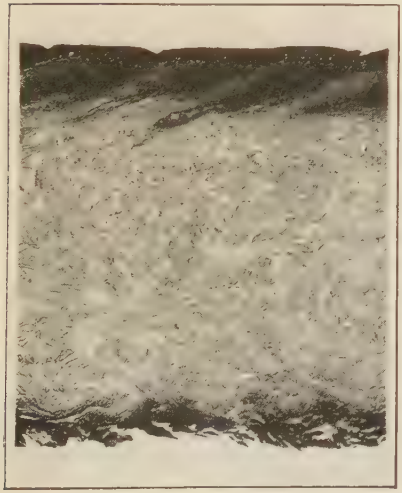


Fig. 7.—Vertical Section of Calfskin (after Chrome Tanning, Coloring, and Finishing), Magnified 75 Diameters.

Courtesy, A. F. Gallun and Sons Co.

Fig. 8.—Vertical Section of Calfskin (after Vegetable Tanning, Coloring, and Finishing), Magnified 75 Diameters.

tions of chromium sulfate. This acid appears to be necessary to the leather, for when it is removed by neutralization the leather becomes brittle. Under the microscope each chrome-tanned fiber looks like a transparent rod of green glass. If the operation is carried out properly there is no precipitation of chromium on the surfaces of the fibers, but only a direct combination of chromium with collagen, which is practically uniform throughout the substance of each fiber. Ordinarily, 100 grams of collagen combine with about 7 grams of chromic oxide (Cr_2O_3). In chrome tanning the collagen fibers combine with only about 11 per cent as much material by weight as in vegetable tanning, which explains the greater fullness and solidity of the vegetable-tanned leather. This can be seen by comparing Figures 7 and 8, page 168, which show cross sections of chrome and vegetable leathers made from opposite sides of the same skin.

Fat-Liquoring and Coloring

If leather is allowed to dry without further treatment, immediately after tanning it becomes very stiff. In order to make the leather soft and pliable, oils are incorporated in it by tumbling the tanned skins in a warm emulsion of oil-in-water. The tiny oil globules cover the surfaces of the leather and during the subsequent period of drying, the oil slowly diffuses through the leather, lubricating the fibers so that they slip easily over one another. This makes the leather pliable and increases its strength.

The leather is then dyed to give it the desired color. This is usually done by putting the skins into a re-

volving drum and pouring the dye liquor on them through a hollow axle in the drum.

Finishing and Mechanical Operations

The skins are finally treated with a sizing material, such as gelatin and casein, in order to give them the desired luster—an operation known as finishing. Incidentally, the skins are subjected to a score of mechanical operations designed to adjust the many physical properties of the finished leather and these require the attention of highly skilled artisans.

Chemical Control

In the tannery whose processes were briefly described, a large staff of chemists is kept constantly at work safeguarding and improving the operations. One group of chemists analyzes all incoming material to insure constancy of composition; another analyzes all liquors and skins at the various stages in order to control and guarantee uniformity of operation; and a third group is constantly seeking new ideas and experimenting in order to improve the processes. Few industries present to the chemist problems which are so complicated as those of leather chemistry, but this very fact makes the leather industry offer unusual promises of reward to the chemist who is outstanding in the fundamental knowledge of his profession.

Enlightening the Public

When an industry grows rapidly, one frequently hears from the consuming public complaints that the product has become inferior. Often this is fancied,

but sometimes it is justified, and it then becomes the duty of the scientific men of the industry to discover the cause and correct it. The leather industry is now furnishing an interesting example of this.

The invention of chrome tanning was hailed by the tanners as a great blessing because it is a much simpler method than vegetable tanning, requiring less time and skilled labor and involving less chance of loss from sudden market changes or from an unbalancing of the operations. The shoe manufacturer, in turn, found it easier to work chrome upper leather into some types of shoes. The result was a gradual shifting towards the chrome process until now more shoe upper leather is chrome-tanned than vegetable-tanned.

That the public had no voice in a change affecting its comfort is not so surprising in that relatively few people know that there are two general and distinct methods of tanning. When chrome and vegetable-tanned leathers are first made into shoes, only an expert can tell them apart. But, in actual wear, the difference is really very great. Shoes made from chrome leather are less comfortable than those made from vegetable leather and they do not hold their shape so well. What many look upon as a degradation in the ancient method of tanning is rather the substitution of a cheaper but very different method of tanning, which yields a leather inferior to the vegetable leather in comfort and resistance to distortion. As a matter of fact, the vegetable-tanned leather made today is superior to any made heretofore, which may be attributed largely to the application of fundamental chemical principles.

The greater tendency for chrome leather to lose its shape is because of its looser structure, as can be seen

by comparing Figures 7 and 8. Vegetable tanning builds the collagen fibers to a much greater size than does chrome tanning and the result is a leather much more resistant to distortion.

Recently chemists have studied the cause of the greater discomfort experienced when wearing chrome shoes and found it was due to the greater tendency for chrome leather to shrink and expand with changing relative humidity of the atmosphere. This property is apparently related to the much higher contents of protein and sulfuric acid present in chrome leather. In one series of tests on calf leathers, with increasing relative humidity from 0 to 100 per cent, chrome leather was found to increase 18 per cent in area and vegetable leather only 6 per cent. In returning to 0 per cent relative humidity, corresponding shrinkages occurred and the whole operation was found to be quantitatively reversible.

In order to show the universal nature of this difference, samples of leathers were procured from various parts of the world and all showed the same difference in properties. The extreme values for area change found were 5.3 to 7.7 per cent for vegetable leathers against 15.1 to 23.0 per cent for chrome leathers. The increase in area is brought about by the absorption of water from the atmosphere.

In series of wear tests, the writer has worn a chrome shoe on one foot and a vegetable shoe on the other. With changing relative humidity, the changes in size of the vegetable shoe have always been relatively insignificant, whereas the chrome shoe invariably became too loose in damp weather and caused a sharp pinching with a drop in relative humidity. It was thus made plain that the secret of forecasting weather by the degree of pain in one's corns lies in the changing size

of the shoe with changing relative humidity of the atmosphere.

Chrome leather was found undesirable for army shoes because of the discomfort they caused, but the World War found the tanners unprepared to make vegetable-tanned leather in sufficient quantity. The result was the compromise army upper leather, consisting of chrome leather partially retanned with vegetable extracts, but which was not so good as a pure vegetable leather.

In such a situation, relief must come either from the tanners themselves or from an enlightened public. The public can demand vegetable leather and get it or the tanner can do one of two things: return to the old method of vegetable tanning, lessening his risks through scientific control; or conduct research work intensively with the object of removing the objectionable properties from chrome leather.

Opportunities for Chemical Research

Upon entering the leather industry, the chemist sees pass before him an endless chain of problems which appear more or less baffling at first glance, but whose solution offers such great promise of reward as to stimulate his determination to solve them.

He naturally hesitates to accept a procedure requiring six months for the conversion of unhaired steer hide into sole leather. Chemical reactions are usually very rapid, so why should it take months rather than minutes to bring about the combination between collagen and tannin? The apparent answer is that the tannin must come into contact with the collagen before it can combine with it and that tannin diffuses throughout the substance of a hide ever so slowly.

But the chemist has already discovered that this rate of diffusion can be increased many times by suitably adjusting the acidity of the tanning liquor or by adding certain nontanning materials. A change of acidity, on the other hand, involves other factors which may affect the quality of the leather. However, the work which chemists have already accomplished has opened the way for a series of investigations that seem certain to bring about that great decrease in time and labor which many tanners of heavy leather claim will turn present deficits into substantial profits.

In the beamhouse work, too, it may be asked why it takes many days and so much handling to get rid of the undesirable portions of the hide. Why cannot some material be used which will quickly dissolve all material except the collagen fibers used in making the final leather? In all probability some means of bringing this about will be discovered by some enterprising young chemist who has the initiative and the persistance to see it through.

The work described here dealing with the comfort and appearance of shoe upper leathers has opened up a wide field for service to the public as well as for profit. Comfort, appearance, wear resistance, and many other properties are determined by the chemical composition of the leathers, which chemists have only just begun to study. Fascinating problems might be mentioned in connection with practically every operation employed in making leather, many in virgin fields of industrial research.

For the student contemplating taking up leather chemistry as a life work, it may be said that the industry offers seemingly infinite possibilities for fruitful research, but that the tool most urgently required to

succeed in such work is a thorough mastery of the fundamentals of pure chemistry and physics.

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CHAPTER XIII

NONFERROUS METALLURGY

H. W. Gillett

Chief, Division of Metallurgy, U. S. Bureau of Standards

Nonferrous metallurgy is concerned with all metals other than iron. It is no small subject either in scope or in importance. There are fifty well-known nonferrous metals.

An alloy is a mixture of two or more metals. Many of the nonferrous alloys contain three or four metals. A recent list of nonferrous alloys dealing only with alloys of the more common nonferrous metals includes over sixteen hundred of more or less definite commercial use.

Importance of the Nonferrous Metals

This chapter is to deal with the more important nonferrous metals. When one tries to classify them in the order of their importance, copper comes first, because all electrical apparatus, lights, the telephone, the radio, automobile ignition, and everything run by an electric motor requires copper wire to carry the current. Up to the middle of 1924, five million pounds of copper had been used in radio sets. In the single year of 1923, one hundred and seventy million pounds of copper were used in automobiles, and over one billion pounds were used in electrical apparatus, i.e., nearly ten pounds of copper a year for each per-

son in the United States goes into the electrical industry. The amounts of the other nonferrous metals used are smaller than in the case of copper, but they are all large.

Because of its lightness, aluminium is essential in aircraft and in automobiles and cooking utensils. Nickel for nickel-plated articles, such as automobile radiators and faucets, and zinc for zinc-coated articles, such as fence wire, are certainly essential to prevent rust. Zinc is also required for dry cells, such as in flash-lights. Without tin for the coating on tin cans, all of our canned foods would have to be packed in fragile glass or some other more expensive container. The dairyman would have to find a substitute for the big cans in which he ships milk.

Lead is required for storage batteries. The hunter and the fisherman will insist that lead shot and lead sinkers are essential to them.

The housewife would class silver as important, for she would not like to do without her silver spoons and forks. We might get along with silver coins if we had no gold, but most people prefer a gold watch.

The chemist could not carry out some of his analytical work without platinum dishes, so he would call that metal essential. We will all admit that tungsten is essential in the electric light, because the tungsten lamp gives us better and cheaper light than we can get from the old carbon lamp. Mercury is useful in thermometers.

Besides these, we need arsenic to harden lead for shot, antimony to stiffen lead for storage batteries and to add to lead and tin for type metal with which to print our books and newspapers. Silicon and magnesium, as well as copper, are required in the aluminium alloy used in airships. We have to use

chromium as an alloy with nickel in the heaters of electric toasters and flatirons. Manganese in small amounts is very useful in a number of alloys.

The seventeen nonferrous elements we have named are the most important and of these, copper, tin, zinc, lead, aluminium, and nickel are the most common. A pound of tin or nickel is usually worth about 35 cents; one of aluminium about 25 cents; one of copper about 15 cents; one of lead or zinc about 7 cents.

Separation of Metals from Their Ores

With the exception of gold, of a small part of the copper, and a still smaller part of the silver, these metals are not found in Nature as the metals themselves. They are found as chemical compounds of the metals. The metals have to be separated out of these compounds.

When there is sufficient metal in a rock or other mineral to make it pay to separate the metal, the mineral is an ore. The place from which the ore is dug is a mine. In iron mining half the weight of the ore has to be iron to make it a good ore, but copper or nickel ore with less than 2 per cent of the metal are worth mining. Lead and zinc ores have to contain more metal, or some gold or silver which can be recovered. In nonferrous metallurgy, therefore, we often have to handle 90 to 98 per cent of material that we do not want, in order to separate the 2 to 10 per cent that we do want.

Nature seldom gives us only one metal in an ore, though some tin ores in the Malay Peninsula have been washed down the streams and separated so that the ore can be taken out of the stream and quite simply converted into very pure metal. But the metals

are generally mixed with other metals in the ores, and they may be combined with some element that must be removed entirely. A nickel ore, for example, may contain 1 per cent of copper, 2 per cent of nickel, a little cobalt, and some manganese, a lot of iron, and say 30 per cent of sulfur. From this we have not only to separate the copper and nickel from iron and from each other, but the copper must not contain more than one part in three hundred thousand of sulfur and the nickel almost as little. To get a thousand pounds of copper and nickel from such an ore, we have to get rid of ten thousand pounds of sulfur, leaving only one-tenth of a pound of sulfur with the metals. (Of course the chemist will generally save some of this sulfur by making sulfuric acid out of it.)

Most nonferrous metals have to be very pure indeed. There should not be over one part in one hundred of all other elements in aluminium, not over one part in one thousand in lead or tin, not over five parts in ten thousand in copper, and not over one part in ten thousand in silver. Some elements have to be kept out almost entirely. One part of bismuth in twenty thousand will make copper so brittle that it cannot be rolled or drawn into wire. The metallurgist has to use chemistry to find, by analysis, just what chemical elements or compounds are in the ores, in what amounts they are present, and what impurities are left in the metal. When he mixes (that is, "alloys") two or more metals together, he may have to analyze the mixture to be sure he has it right. Chemical laboratories are necessary for control of all the smelting and melting processes in which the composition of the metal is changed. At one smelting plant the chemists make sixteen thousand chemical analyses each month.

The metallurgist makes use of all sorts of differ-

ences in the behavior of the elements and of their compounds in separating the metals from the ores. He may grind the ores and shake them with water to float off the compounds he does not want. Or he may add to the ore a very little of an oil which will stick to the particular metal compound he is seeking, stir the ore up with water and blow in air, which sticks to the oil and floats up the oiled part of the ore, leaving the rest behind.

By such methods he concentrates the ore so as to get less of the waste rock, sand, etc., which he does not want. The concentrated ore then has to be treated chemically to separate the metal. This process is called smelting. We melt a metal, and it is the same after melting. But we smelt an ore, i.e., we change it chemically, freeing the metal from the other elements with which it is combined. Smelting generally involves melting.

The chemistry of the smelting processes differs with the different metals and with the different elements and impurities in different ores. It would take too long to go into the details of the smelting of our six most common nonferrous metals, to say nothing of all the others, so we can only indicate the general methods used. Smelting is done by two chief methods, one using fire and the other, electricity.

Fire Smelting

Fire-smelting methods depend on the fact that the carbon in fuels, such as coal, coke, or charcoal, readily burns with the oxygen of the air to form a gas containing both carbon and oxygen. This is called carbon monoxide, i.e., carbon with one part of oxygen. In burning, carbon gives off heat. Carbon will also take

the oxygen from a compound of a metal and oxygen (i.e., a metal oxide, like copper oxide) to form the same gas, carbon monoxide, if the metal oxide and the carbon are heated sufficiently hot. The gas carries the oxygen away and leaves the metal as metal. This process is termed "reduction." The temperature is usually high enough to melt the metal.

If we let sufficient air into a furnace in which we have the fuel and the metal oxide, we burn part of the fuel to get heat. The rest of the fuel is there to combine with the oxygen of the metal oxide. Thus, we get at the same time the necessary heat to make the oxide willing to give up its oxygen to the carbon and the carbon willing to take up this oxygen.

If we try to make metallic silicon from sand (which is the oxide of silicon called silica), we cannot get the furnace hot enough to make the silica give up its oxygen. So we pass an electric current into a special furnace, since the electric furnace can get much hotter than a furnace in which fuel is burned. The electric current used is an alternating current, such as we use for electric lights, and all the electricity does is to heat the furnace. For most metals, however, we can get the furnace hot enough by burning coal or some other fuel.

Not all ores have the metals as oxides only. The metal may be combined with sulfur, as in the nickel ores previously mentioned, or it may be combined with both oxygen and carbon dioxide, as in some zinc ores. Carbon dioxide is the gas in the bubbles in soda water. It is carbon united with two parts of oxygen instead of with one, as in carbon monoxide.

If the metallurgist does not have an oxide ore with which to start, he has to change it into the oxide. When the metal is combined with sulfur, some of the sulfur

will often come off by simple heating. The rest can be burned off by high heating and blowing air over it, or sometimes through it. The illustration facing page 182 shows a furnace or converter through which the air is blown. The sulfur burns to a gas containing sulfur and oxygen; the gas goes off, but the metal is not left as metal because we are using oxygen to get rid of the sulfur, and the metal at once combines with more oxygen. But now we are rid of the sulfur and have the metal oxide ready for smelting with some form of carbon.

If the metal in the ore is combined with both carbon dioxide and oxygen, the carbon dioxide can often be driven off as gas by heating and the oxide left behind. This heating could be done in the furnace in which the resulting oxide is to be smelted. But then the carbon dioxide would use up a lot of the carbon in the fuel, since it would give up half its oxygen to form carbon monoxide with the carbon of the fuel and would itself also become carbon monoxide. This would be a waste of fuel, so the ore is heated to drive off the carbon dioxide before it is put into the smelting furnace.

Thus every step of the smelting process depends entirely on the chemical behavior of the ore with which we start.

The treatment of the ore in smelting also depends on the chemical behavior of the other materials present that we do not want. It is very seldom that this unwanted material will melt readily of itself, so other materials, called fluxes, have to be added to make it melt down to slag. Slag is a mixture of nonmetallic chemical compounds that will melt at the proper temperature. In many ways it is a good deal like glass.

Choosing these fluxes is another chemical problem, which is different, not only for every metal, but for

Courtesy, International Nickel Co.

Converter Furnace for Smelting Copper or Nickel.
Notice the size as shown by comparison with the man in the photograph.

almost every different ore. The fluxes not only have to be chemically suitable, but they have to be cheap, because the slag they form is usually of no use and has to be thrown away. The illustration, page 184, shows molten slag, from the smelting of nickel, which has been drawn off into huge pots, being poured on the dump.

In the fire smelting of zinc, the mixture of ore and coal has to be heated so hot before the metal is released from the oxide that the separated zinc not only melts but actually boils, and the metal has to be condensed from its vapor just as water condenses from steam. If the temperature is not correct at the point where the zinc is to be condensed, and if some gas is present that will combine with zinc, the zinc will condense in tiny drops instead of to a pool of molten zinc. It is hard to get the drops to join together so that they will freeze into good solid zinc. In order to control the temperature and the other conditions it is necessary to smelt zinc in quite small containers called retorts. Hundreds of these retorts are used over one fire. So while the individual retorts are small, each one holding less than one hundred pounds, the furnace as a whole is large. Most of the other common metals are smelted in huge furnaces, because it costs less per ton of metal to work on a big scale.

Some blast furnaces are almost as tall as a church steeple. The inside of a furnace for smelting copper is often 120 feet long by 20 feet wide. Such furnaces melt hundreds of tons of ore in a day, and instead of putting in a shovelful of coal at a time, a couple of tons will be added.

The chemical reactions of smelting have to be carried out at very high temperatures and the furnace has to have a lining which will not melt. It would

take too long if we had to put a new lining in such big furnaces every few days. The furnaces often run for years without stopping. So the metallurgist has to get the ceramic chemist to provide fire bricks for lining the furnaces that will not melt at the temperatures used or be affected by the ore or fluxes used. (Ceramics deals with products made from clay and like materials, such as brick, fire brick, china, spark-plug porcelains, etc.) The chemical problems brought to the ceramic industry by the metallurgist are many, and a good deal remains to be done in solving them. If we could get suitable fire brick, we could do a lot of things with ores and metals that we cannot do now because we cannot get anything that will hold the materials we want to use at the temperatures we would have to use. Or, if we can get it, we cannot get it cheaply enough.

There are many unsolved problems connected with the smelting of ores. In some ores there are so many metals and so many different kinds of waste materials which must be separated, that the smelting and purification is too expensive a job. This is the case with some complex ores of zinc. Zinc ores are getting scarce and the chemist who is ingenious enough to figure out a cheap way of using these complex ores will do the country a service and, incidentally, make money. Most of the metals smelted by fire are rather impure and have to be remelted and purified in various ways, the chemistry of which it would take too long to discuss here.

Smelting by Electricity

Instead of smelting by heating the oxide of the metal with carbon, we can sometimes treat an ore with acid

Courtesy, International Nickel Co.

Pouring Furnace Slag on the Dump.

and water, and dissolve the metal as a salt. If we put sulfuric acid on a copper ore that contains its copper combined with oxygen and carbon dioxide, we drive out the oxygen and the carbon dioxide. At the same time we lose part of the acid, which combines with the oxygen to form water. The rest of the acid combines with the copper to give a salt—the blue copper sulfate found in every chemical laboratory. This blue salt dissolves in water, so when we mix the ore with water and the acid, we get the copper as this salt dissolved in water. We can pour it off the sand which was mixed with the copper in the ore, for the sand does not dissolve.

Next we take such a solution of a salt of a metal and put into that solution something that will carry the electric current into the solution, but will not dissolve in the solution. This is called the anode. Then we need something that will carry the current out of the solution. This is called the cathode. We are then ready for another sort of smelting process. Electric current (not the kind used in electric lights, but the kind we get from a storage battery) is passed through this arrangement. The metal in the dissolved salt of the metal is made to move along by means of the electric current and when it gets to the cathode it will separate from the solution and "plate" out, or deposit, as metal on this object we call the cathode. The part of the acid that was joined to the metal in the dissolved salt moves along in the other direction, and when it gets to the anode it combines with water. By taking up the hydrogen of the water and setting free the oxygen of the water as gas, it forms with water the acid with which we started in treating the ore. This acid is used to dissolve more copper from the ore. So the acid is used over and over.

In this process we are getting metallic copper and oxygen gas, just as much copper and just as much oxygen as we took out of the original ore in the form of copper oxide. By thus going around Robin Hood's barn with acid and electricity, we separate oxygen and metallic copper, which is exactly what we did in a different way in the fire-smelting process, though then when the oxygen came off it was combined with carbon as carbon dioxide. One of the principal advantages of the electric process (or electrolytic process as it is called) is that when the metal is thus separated by electricity a much purer metal is produced.

When we smelt the ore with carbon many other metals come out with the copper. But when we treat the ore with acid, some of them stay behind. The acid solution is then treated with other chemicals to remove some of the things we do not want. And when the electric current passes, some of the metals that would come out of these oxides on heating with carbon do not deposit with the copper but stay in the solution.

Thus another branch of chemistry, electrochemistry, is used by the metallurgist. The electrolytic process is quite new in its use on ores, but it is used on some South American copper ores and the copper so made costs much less to separate from the ore than that made by fire smelting. This process will not work on the ores in which the copper is combined with sulfur because copper so combined will not dissolve in a cheap acid.

Some zinc ores are treated in a similar way. This helped greatly during the World War. When zinc is made in the usual way, some lead goes along with the zinc if the ore contains lead. Lead in zinc makes it difficult to form a perfect cartridge case from brass

in which the zinc is used. Cartridge cases were needed, but enough zinc ore that was free from lead could not be obtained. The electrolytic method was used on zinc ores containing lead and gave pure zinc.

There is a good deal of chemistry involved in the making of zinc by the electrolytic method. Very tiny amounts of some elements in the solution will keep the method from working properly. One part of arsenic in a million will spoil the process. Careful chemical purification of the solution is therefore necessary.

Pure aluminium cannot be made from its ores by smelting the ores with coal or coke. Neither can aluminium be deposited by electrolysis of solutions of its salts in water. So the ore is chemically treated to change it into the oxide of aluminium and, at the same time, purify it from the other materials in the ore. The oxide is then fed into a pot full of a red hot, melted mineral. This mineral, a compound of aluminium, is rather rare and has to be brought from Greenland. Material of the same composition made by the chemist can also be used. Electric current is then passed through the contents of the pot, just as in depositing other metals from their solutions in acid and water. But the temperature is so high that instead of being deposited in solid form, as is the case with nickel and the other metals, aluminium comes out melted.

Electrorefining and Plating

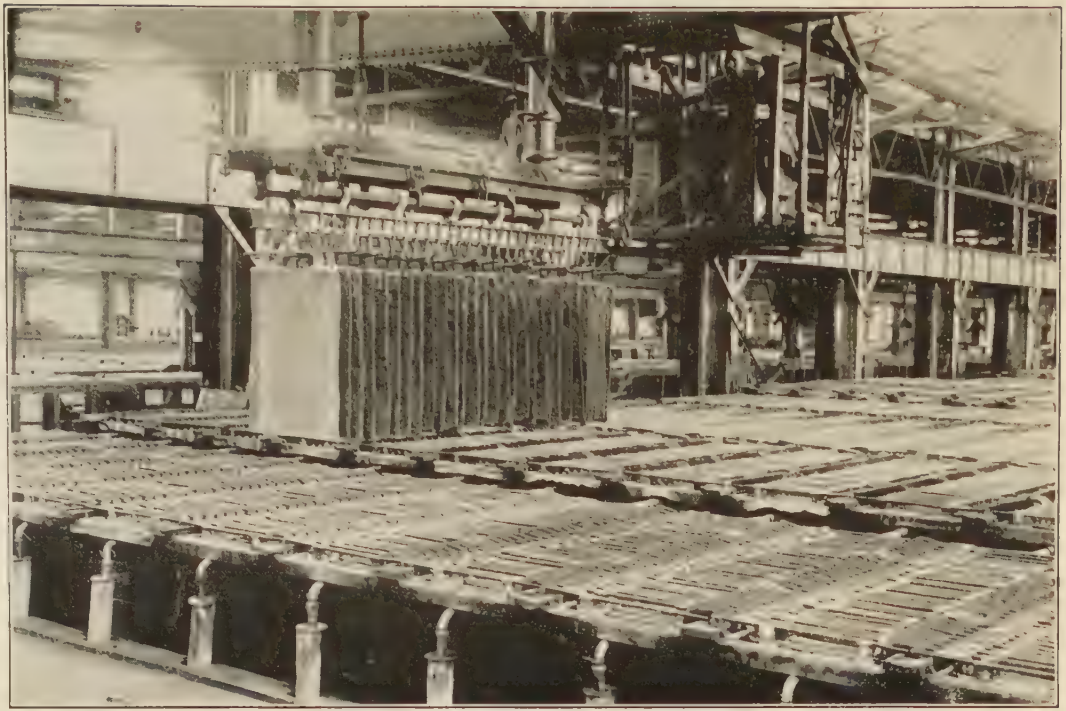
In the electrolysis of copper and zinc solutions obtained from the ores, it will be remembered that the anode through which the electric current entered the solution was one that would not be dissolved. The

anode used may be an alloy of copper and silicon in just the right proportions, as this is not dissolved. If we leave out the silicon and use a copper anode, such as one made from the impure metal by fire smelting, this copper will dissolve, and we can thus move the metal along from the anode to the cathode. (These words, "anode" and "cathode," are each made from two Greek words. The "*ode*" means "road," i.e., the path by which the current gets in or out of the solution. The "*an*" means "from" and the "*cath*" means "to." The metal moves *from* the *an*ode to the *cath*ode.) But the silver which often occurs with the copper ores and which goes along with the copper through the fire-smelting and fire-refining processes does not dissolve. Silver drops off the anode and can be taken out, dissolved in another kind of acid, and itself electrolyzed to give the metal.

The extra value of the purer copper obtained by electrolysis and the value of the silver recovered more than pay for the cost of electrolysis. So most copper that is made from the sulfide ore by fire-smelting is finally purified by electrolysis. Many other metals can be similarly purified.

Electrolysis also makes it possible to deposit a thin coating of copper, zinc, nickel, silver, gold, etc., on iron, steel, or other metals. This is called plating, and gives us silver plate, nickel plate, gold plate, etc. Much jewelry is gold plate instead of solid gold.

Zinc and tin can be put on in the same way, but they are more often put on by melting them (since they both melt at fairly low temperatures) and dipping the metal object to be coated in the molten metal. A thin layer of the zinc or tin sticks to the object and on taking it out the layer freezes.



Courtesy, Raritan Copper Works.

Electrolytic Copper Refinery. Cathodes being taken out of the Electrolytic Bath.

Nonrusting Properties of the Nonferrous Metals and Alloys

These coatings, whether obtained by electroplating, by dipping, or by some other methods, are of vast use to mankind in preventing the rusting of iron and steel.

A thin piece of iron, like a stovepipe, will soon rust and be useless unless it is covered so that air and moisture cannot get to its surface. The blade of a steel knife will rust tight if the knife drops out of one's pocket and stays out in the rain or dew a few days. Automobiles, steel bridges, and all iron or steel articles have to be covered with paint or enamel to prevent rust from eating and spoiling them. Rusting goes on and on until it will finally eat through the iron or steel.

Rust can be fought by taking great care to get very pure iron, but such iron is not very strong. Iron has to contain carbon to change the rather soft iron into the harder steel. Rust can also be fought by adding a little copper or a great deal of chromium. Chromium gives stainless steel, and knives made of stainless steel are getting to be common. But stainless steel is pretty costly. To fight rust it is best to make things out of some nonferrous alloys or to cover the iron or steel with one of the nonferrous metals.

Now, as a matter of fact, these nonferrous metals and alloys do get covered with a sort of rust. Iron rust is iron chemically combined with oxygen and moisture from the air. All the nonferrous metals combine with oxygen in the same way, some of them even more easily than iron. A bronze statue will in time get dark through the formation of such a coating. If

you rub an old penny on a piece of cloth or a carpet for a minute or two, you can rub off the coating and the penny will again be bright. Lead takes on a dark coating. But the white metals—tin, aluminium, and nickel—do not get dark because the coating is so thin one can see through it as if it were not there.

The difference between the iron rust or oxide and the rusts or oxides of the nonferrous metals is that the latter are thin and stick tight like a good coat of paint. They do not let more oxygen through to eat the metal beneath. Iron rust, on the other hand, is loose and porous. It flakes off and not only lets the oxygen through but actually makes it combine with the iron faster than it would if the rust were rubbed off.

Coatings of copper, nickel, or tin keep the air and the moisture away from the iron and prevent it from rusting. When they finally wear away, the iron thus bared will of course rust. With a coating of zinc, however, a small bare spot will not rust because the iron, the moisture of the air, and the zinc make up a little electrolytic cell somewhat similar in nature to the cells used in flash-lights, in which the zinc will dissolve instead of iron. So unless the bare spot is too big the zinc continues to protect it, while with the other coatings the attack upon a bare spot is hastened. Thus the chemical difference between the metals affects the choice of a metal for coating iron to protect it against rust.

The best way to avoid rust, though not always the cheapest unless we have an article that must last a very long time, is not to use iron at all, but to make the whole article of a nonferrous alloy. The chemical difference between iron and the metals under consideration is the reason for making so many things of brass

Courtesy, Raritan Copper Works.

Electrolytic Copper Refinery.

Compare the size of the man by the window at the right. This is large scale chemistry. How many pennies would the copper shown here make? The copper in the tanks in this photograph is worth about half a million dollars.

or other nonferrous alloys when they could just as well be made of iron provided it would not rust.

The nonferrous metals all cost more than iron because Nature has given us lots of iron in a form fairly easy to separate into the metal. The other metals are either not so common or else are locked up in chemical combinations which make it more expensive to separate and purify them. But iron and steel are stronger than most of the nonferrous metals. So we get the strong inside by using steel and the nonrusting outside by coating the steel with some nonferrous metal. Or we can coat a cheap metal, such as brass, with a better-looking but more expensive metal such as nickel. Not only these coatings of pure metals, but the nonferrous metals and alloys in general, are much more resistant to the action of acids and chemicals than are iron and steel. While some of these nonferrous metals and alloys may dissolve in a given chemical or acid, others can usually be found that will not. Thus, in canning, many food products are cooked in copper, nickel, or aluminium pots; varnish is prepared in copper caldrons; and so on.

Many other branches of chemistry are thus helped by the noncorroding properties of the nonferrous metals.

Forming

Metal can be drawn into wire by pulling a rod of it through a small hole in some harder material. This can be repeated, using smaller and smaller holes to get different sizes of wire. The tungsten wire in the filament of a flash-light is so fine one has to look hard to find it. Some sizes of copper wire are regularly made in mile lengths. Metal can be rolled into sheets

by squeezing it between rollers, like those of a wringer only much larger and made of steel instead of rubber.

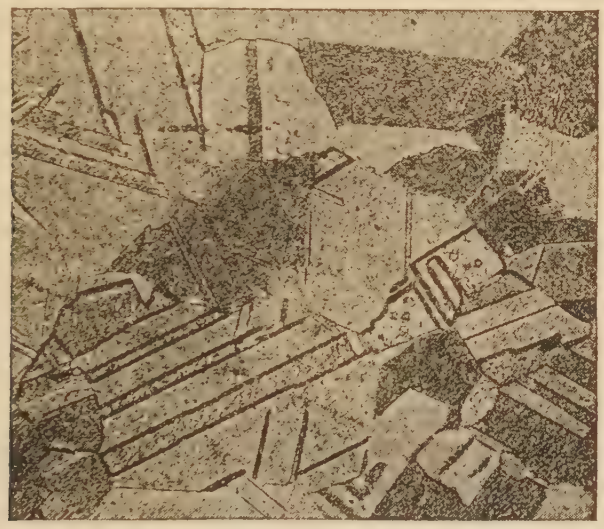
Some metals have to be heated for drawing or rolling, while others can be worked cold. In the process of cold-working the material is made harder and stronger, because the crystals of which the metals are composed are crushed into smaller ones. Metals made of small crystals are stronger than those in which the crystals are large. If the metal which has thus been strengthened is heated to the proper temperature, the crystals in the metal grow in size, several little ones joining to form a big one, and the metal gets soft again. Hard-drawn copper wire is quite stiff, but if it is heated or annealed it can be bent very easily.

Brass, an alloy of copper and zinc, is so much affected by the size of the crystals that the easiest way to tell the maker of brass just how hard the alloy should be is to tell him how big the crystals should be. That metals are crystalline can be realized by looking at the zinc coating on a garbage pail. This shows the spangles caused by the zinc freezing in big crystals, much like the frost crystals on the windowpane.

In most metals and alloys the crystals are very small and have to be magnified one hundred or even one thousand times by the microscope to make them show plainly. The metallurgist uses the microscope to tell him more about the metals than he can tell with the naked eye. The illustration on page 193 shows a photograph, taken through the microscope, of a piece of brass that has been cold-worked and then annealed.

Besides drawing into wire and rolling into sheet, metals can be formed by squeezing them out of a hole while hot (extrusion) or hammering them into the shape desired (forging). Very often, however, it is easier to get the metals into the size and shape desired

by melting them. A hole is made by packing damp sand about a pattern of the desired shape and size and then withdrawing the pattern. The liquid metal is poured into the hole in the sand. The metal then freezes into shape.



Brass, magnified 250 times. This shows that metals are made up of tiny crystalline grains

None of these methods of forming metals and alloys gives the exact size needed, so the final form is given by cutting (machining) it into shape. Of course metal is pretty hard to cut and considerable care often has to be taken in choosing an alloy to see that it will machine easily. Lead is added to brass to make it cut more readily.

Alloying

We have pointed out the great care that is taken to separate the metals from their ores and from any im-

purities that may be present. But for many uses the pure metals are too soft and too weak. They can be hardened somewhat, as we have said, by cold-working, but the chief method of hardening and strengthening the metals is by mixing them together in an alloy.

Some of the alloys are very different from the metals that enter into them. Copper is red, and quite soft and weak. Zinc is whitish, weak, and rather brittle. By melting together, i.e., alloying, two parts of copper and one part of zinc we get brass, which is yellow, strong, much harder than copper, and much less brittle than zinc. Tin is white and soft. When one part of tin is mixed with nine parts of copper the resulting alloy, bronze, is brown, hard, and strong.

We may vary the amounts of zinc in brass, and of tin in bronze, and thus change the way the alloys behave. Up to about 45 per cent of zinc or 12 per cent of tin, these alloys are useful, but if we go just a little above those figures we get very brittle alloys. To explain this, we have to go to still another branch of chemistry, called physical chemistry, which deals among other things, with the way the alloys of different compositions behave at different temperatures. The physical chemist measures all sorts of different properties of the alloys, looks at them with the microscope, and finds out at what compositions and temperatures the alloys change. He then draws what he calls an equilibrium diagram, but which can be considered as a map showing the field in which he must stay to get a good alloy.

Sometimes this map shows that by heating the alloy to the right temperature, then cooling it rapidly, and again heating it to a lower temperature, the alloy can be made stronger. This heat treatment is required by

the aluminum alloys used in the framework of the airship Shenandoah. After such treatment the alloy is nearly as strong as steel, though it weighs only one-third as much.

The maps also indicate how the melting point of the metals changes when they are alloyed. Equal parts of lead and tin form solder, an alloy that melts at a lower temperature than either metal alone. The right proportions of lead, tin, bismuth, and mercury give a trick alloy that is solid at the temperature of the air, but melts so low that a teaspoon made of the alloy will melt when put in a cup of hot tea.

A more useful alloy, made of copper, zinc, tin, and a little aluminium, manganese, and iron, is strong enough to be used for propellers of ocean liners. In some propellers, each blade is taller than a man. This alloy is not attacked by sea water, while a steel propeller would rust very soon.

Chemical Improvements in Metallurgy

Metallurgy is largely chemistry. Smelting, refining, electroplating, alloying, heat treatment, and many other steps between the ore and the finished product involve some phase of chemistry, whether it be analytical chemistry, electrochemistry, physical chemistry, or general chemistry. The metallurgist has to be something of a physicist, something of an engineer, and something of a business man, for he deals with problems of physics, of engineering, and of costs. But the one thing he cannot do without is chemistry. He meets chemical reactions and chemical principles at every turn. A thorough training in chemistry is essential for the man who wants to handle metals. Prob-

ably 75 per cent of the metallurgists started as chemists before they entered the fascinating field of metallurgy, and the other 25 per cent had to study chemistry to understand their work.

Much has been done by the chemist in improving and cheapening metals and their alloys. Much remains to be done. There are ores which so far are useless because proper chemical methods have not yet been found for extracting the metals. We do not have a sufficiently cheap method for purifying some metals, nor do we know how to handle some of the less common metals. Really pure aluminium has only been made in very small quantities owing to chemical difficulties. Pure chromium is also rare, and chemists are still groping for a method to make the pure metal ductile instead of brittle. Yet when chromium can be made ductile enough to be drawn into wire, there will be important uses for it.

Metallurgists have recently applied the X-ray and the X-ray spectrograph to metals. The X-rays will pass through a person's body and take a photograph of the shadow of his bones, since they pass through the bones less readily than through flesh. In the same way the X-ray will pass through metals and show the shadows of defects that are present. The X-ray spectrograph applies X-rays in a different way, and makes it possible to tell something about how big the crystals are, and not only that, but how the atoms that make up the crystals are arranged and how far apart they are. The atoms themselves are a thousand times too small to be seen by the most powerful microscope.

The X-rays have only begun to be used, but the little work so far done has told a good deal about how the metals are really made up and why the alloy of two

metals may be harder than either one of the metals. Much more information is expected from this sort of work.

Metals take up gases in melting, and it appears likely that very tiny amounts of gas may make the metals act very differently. So chemists are developing methods to find what these gases are, the amounts present, and just what they do to the metal.

Very few alloys are really strong at very high temperatures, and those that can be so used are expensive. Yet the best methods for making nitrogen from the air combine to form some chemical compound for use as fertilizer require the use of metals at high temperature. There are many other things for which we need alloys of greater strength when hot and the metallurgist will have to supply them.

There are metals, such as cobalt and molybdenum, which are useful but for which few uses have yet been developed that are not met by some cheaper metal. Large deposits of the ores of these metals are, so far, only mined on a rather small scale. When some new use that these metals just fit is found they will be produced on a larger scale and thus made cheaper.

Nickel is in somewhat the same state. Nickel is plentiful but until there are more uses for it, it will be rather expensive, so the firms that produce nickel have a lot of chemists hunting for new uses in the hope that it can be produced on a larger and cheaper scale.

Metallic potassium is seldom used save by the chemist in laboratory work. But very recently a method was worked out for sending photographs by telegraph, and potassium is essential in the apparatus used.

Aluminium used to cost ten times its present cost,

but it became cheaper as new uses were found for it, because more was produced. Now, weight for weight, it costs only about the same as copper. Magnesium is even lighter than aluminium, and some day it will be used almost as widely as aluminium is today.

New improvements are constantly being made in methods and apparatus. In the last half dozen years the makers of brass and bronze have been replacing their old types of melting furnaces with electric furnaces that melt more cheaply and waste less metal in the melting.

What of the Future

In all the advances of metallurgy the chemist has done, is doing, and will do most of the work. As we said at the start, his work on nonferrous metals and alloys makes possible in their present form such things as modern plumbing, tin cans, the automobile, airplane, airship, steamship, locomotive, trolley cars, telephone, radio, electric light, and all other electrical apparatus.

New inventions as important as these, even the names of which we do not yet know, will come. When they do come, they will be of as much use to mankind as these others are now. These new inventions will require new alloys, new improvements, and more knowledge of the nonferrous metals. Chemists who will develop these new alloys, make these new improvements, and acquire this new knowledge are now growing up, though they may not yet know they are going to be chemists and metallurgists. To any such chemists-to-be who may read this chapter, the writer offers his congratulations: first, because their work will be a service to mankind; and second, because they will have a mighty interesting job.

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CHAPTER XIV

CHEMISTRY OF PACKINGHOUSE PROCESSES

W. D. Richardson

Chief Chemist, Swift & Co., Chicago, Ill.

The animal body is past all comparison the most complex organization in gross and in detail known to man. On the basis of a minimum of knowledge and considerable imagination, the ancient chronicler took notice of the fact in the expression, "I will praise thee; for I am fearfully and wonderfully made." Modern science has expanded this vague conception and has opened unlimited vistas of investigation in every direction. Each extension of knowledge has, however, placed the goal of complete information farther and farther away.

The packing industry for the most part considers the animal body in its simpler and more superficial aspects, with the exception of those by-product branches which manufacture gelatin, fats, various enzymes of digestion, extracts of glands, and hormones.

Although the immediate evolutionary ancestors of mankind were probably chiefly vegetarians, living on a diet of fruits, nuts, shoots, and vegetable matter, with only a small proportion of animal food, man has become so largely carnivorous that animal proteins are an essential part of his diet. Without animal proteins

experimental omnivorous animals (white rats) do not thrive and therefore lose in fertility. All the evidence tends to show that the human animal cannot thrive on a vegetarian diet alone, although there are extreme examples, such as some Eskimo tribes, who live entirely on animal foods. Hence, the importance of meat in the diet.

Beginnings of the Packing Industry

The packing industry was foreshadowed in the most primitive times by the processes used by tribesmen in all parts of the world for the preparation of meat. Man, the hunter, brought home the animal from the chase, skinned and dressed it, and then separated the edible from the inedible, the useful from the useless parts. For him the latter were few in number and all but negligible in quantity. Some parts were eaten fresh, either raw or cooked; other parts were dried; still others were salted or salted and smoked; while some, under suitable climatic conditions, were frozen and preserved in this way. The long bones were broken open for the purpose of extracting portions thereof, and the softer bones were pounded in a mortar and probably mixed with soup or stew. Thus an ample supply of calcium phosphate from the bones was insured in the diet, and with iron from the blood the most important minerals were thus supplied to the primitive man's diet. This is an interesting contrast to the diet of modern man, which is frequently lacking in calcium, phosphorous, and even iron.

Ancient man had discovered the four methods of food preservation—namely, by desiccation, by heat,

by freezing (or low temperatures), and by the use of antiseptics (salt and smoke), long before the commencement of written records. These processes are still in use for the preservation of meat food products, although today they are much elaborated and under strict mechanical and scientific control. The carloads of ice and salt and the cords of hardwood received by large packing houses daily attest the antiquity of some of the preserving processes still in use.

After the hunting stage of man, other steps were necessary in the evolutionary development of husbandry and civilization before even a simple abattoir or packinghouse could be considered. First there was the domestication of animals (which probably originated in the desire for pets), and the keeping of more or less extensive flocks and herds. Second, nomadic shepherding had to give way to localized husbandry and great consuming centers had to develop at a distance from producing centers before large-scale meat packinghouses could be established.

Before the Civil War the cities of America which had not reached great size were abundantly supplied with meat from the surrounding farms, the animals being slaughtered near by and the meat being quickly sold and consumed. Certain products, however, principally pork, were salted and packed in barrels and hence the name "packing industry" became applied at first locally and then generally. In the southern part of the United States the word "packery" is used in place of "packinghouse."

The chief distinctions between the simple country slaughterhouse and the modern packinghouse are the following:

Simple Abattoir	Packinghouse
Small-scale operations	Large-scale operations
Insanitary buildings and conditions	Sanitary buildings and conditions
No government inspection	Government inspection
Scant use of water	Liberal use of hot and cold water
Limited natural ice refrigeration	Mechanical refrigeration
Seasonal killing and curing of pork	All year killing and curing of pork
Few by-products saved	All by-products saved
Localized distribution	Large radius of distribution
No scientific control	Scientific control of processes and products
No scientific research	Research leading to new processes and products

The common saying is that in the modern packinghouse everything is saved except the squeal, the moo, and the bleat. Operations take place throughout the year because of mechanical refrigeration, whereas formerly the curing of hams and the making of sausage could only be managed during the cold weather, which idea still persists in ordinary farm practice. The chill rooms and freezers of the large establishment are maintained at uniform temperature from season to season and year to year, no matter what the outside temperature may be. This plus scientific control insures a uniformity of product which was impossible in the early days or in small establishments. Research is constantly improving old and initiating new processes and products.

Thus the packing industry was an old-established empirical industry before the advent of modern science. It was full of good and bad practices and traditional procedure of all sorts, some of which required correction or elimination, all of which required modernization and expansion. The sequence of the hunter and his game, the domestication of animals, the nomad with his flocks and herds, the husbandman and settled agriculture, the opening through exploration of new and fertile grazing lands apart from the old centers of civilization, the continued segregation of con-

suming and producing areas, the small community with its seasonally operated abattoir, the larger establishment with natural ice refrigeration, and, finally, the large centralized establishment equipped with mechanical refrigeration and well-insulated chill rooms, together with machinery for the conservation of by-products—all give the necessary background against which the scientific man and particularly the chemist operated. Today all the large American packinghouses are operated under close chemical supervision and control. In Europe the methods used are primitive and operations are on a small scale only.

Mechanical Refrigeration

The modern era of packinghouse development and operation began in the nineteenth century in the eighties, when so-called mechanical refrigeration was practically developed to such a point that it could be introduced into the industry on a large scale to supplant the natural ice refrigeration previously used and which had been found to be of limited applicability. The change came about gradually, however, and for many years natural ice refrigeration and mechanical refrigeration were used in parallel, until the latter finally supplanted the former altogether, except in the case of refrigerator cars and the smaller distributing markets known as branch houses.

Briefly, mechanical refrigeration consists in the production of low temperatures by the boiling of a liquefied gas, such as ammonia, carbon dioxide, sulfur dioxide, and others. The liquefaction is kept up continuously by means of a compressor (or the equivalent in the case of the so-called ammonia absorption system), so that a cycle of compression, expansion, and recooling of

the gas used, followed by recompression, is maintained. Ammonia is the gas most commonly used in refrigerating plants and may be applied to the chill rooms through direct expansion coils, or may be used to reduce sodium chloride brine (for chill rooms) or calcium chloride brine (for freezers) to a low temperature, these then being pumped continuously through coils in the rooms where beef, pork, and other perishable products are chilled or stored.

In connection with refrigeration, the chemical laboratory makes certain analyses and tests—such as the examination of liquid anhydrous ammonia for purity and noncondensing gases; the analysis of common salt and calcium chloride for brinemaking (calcium chloride is of two kinds: the one, a commercially pure calcium chloride, a by-product of alkali manufacture by the Solvay process; the other a mixture of calcium and magnesium chlorides derived from the mother liquors of common salt manufacture); the physical testing of various heat-insulating materials, such as cork board, magnesia covering, hair and flax felts, and others.

Many additional physical tests are likewise conducted. For instance, the large packinghouses maintain car shops in which refrigerator cars are built and kept in repair, also general machine shops; they are large purchasers of miscellaneous supplies which enter into construction and manufacturing operations. In connection with these matters, many purchased supplies are examined in a routine way and from time to time are made the subjects of special investigation. The following are included: iron and steel, brass, bronze, babbitt, solder, and other alloys, Portland cement, coal-fuel oil, water and boiler compounds, paints and varnishes, lubricating oils, building, roofing, in-

sulating and wrapping papers, asphalt and pitch, salt, sugar, vinegar and spices, milk and cream, fuller's earth, diatomaceous earth, and bleaching carbons.

General Operations

Packinghouses have no control over their raw material. Cattle, calves, sheep, and hogs raised by farmers, ranchmen, and feeders are brought to the stockyard centers and sold to the highest bidder. They are usually slaughtered within 24 hours from the time of purchase. Cattle, calves, and sheep are usually slaughtered in the same or neighboring departments, but hogs are handled in a separate building or department because of the different methods followed.

On the killing floor the cattle are bled, the blood being pumped to the blood house or carefully caught in pans and carried to the albumin department; the hide is removed and dropped to the hide cellar where it is salted; the head and feet are removed and transferred to the oil house and later to the gelatin plant. The edible carcass is thoroughly cleaned with hot and cold water, after which it is conveyed by endless chain into the chill room. The viscera drop to the offal floor below, where edible portions are separated, cleaned, and transferred to their respective chill rooms; fats are separated and transferred to the rendering departments, intestines to the casing room, and any remaining portions not suitable for human food or for which there is little demand—such as lungs, spleens, and various other parts—are transferred to the tank house, where they are cooked in large tanks, usually under 40 pounds pressure, for a period of about 8 hours. Such portions are graded according to quality. The better quality of product, after

cooking and drying, is ground and made into stock and chicken feed, while the lower grade materials become tankage, which is sold for fertilizer. The tank water resulting from these operations is evaporated in triple effect evaporators, and then dried and mixed with stock feed or tankage. The fatty portions produce various grades of tallow and grease in the rendering tank. It should be noticed that, immediately after slaughter, use is made of either low or high temperatures in order to preserve all packinghouse products. Packinghouse operations indeed may be epitomized as a fight against the destructive forces of bacteria.

Chart 1 shows in schematic form these general operations.

Generally speaking, calf products and by-products are handled similarly to those of beef, but the by-products are naturally limited. Since many calves are sold with the skins attached, there are few hides with which to bother. The heads, when not used for food purposes, together with the feet are handled like those of cattle.

Sheep are bled, skinned, and dressed. The heads and feet yield mutton tallow and mutton oil, respectively, and the residual bones are available for gelatin manufacture. The skin is sent to the wool house, where depilatory is applied and the wool removed. The skins are then drenched and pickled in preparation for shipment to the tannery. The edible offal is naturally less than that of cattle but is separated in much the same manner.

Chart 2 shows in diagrammatic form the disposition of hog products. Hogs are handled somewhat differently from other animals and yield rather more edible product. Also, the disposition is more complicated and varied than in the case of other animals. The

hogs are swung up on a rail, stuck and bled, scalded and scraped (for removal of hair), opened and eviscerated, and the head removed. The viscera are washed, separated, and handled separately. A very considerable portion of the hog is converted into edible product of one kind or another. Lard is the principal by-product, leaf lard and back fat commanding the highest price. Tongue, heart, liver, feet, and kidneys are edible, while the intestines, bladder, and stomach serve as sausage casings. The blood goes into animal food and fertilizer. Hair and bristles are made into curled hair and brushes. Pepsin and pancreatin are made from the stomach and pancreas. The dressed carcass is chilled for 48 to 72 hours, after which it is cut into the principal edible parts—hams, shoulders, bellies, fat backs, loins, etc.

In the early days of packinghouses, by-products or their raw materials were thrown away, wasted, buried in the ground, or disposed of by any suitable means. Later in the development, even after mechanical refrigeration was introduced and modern methods were used in the main line of manufacture, by-products were given away. Around each large packing establishment there developed fertilizer works, glue factories, gelatin factories, lard refineries, margarine factories, and other industries to utilize the by-products of the main industry. These establishments required chemical laboratories for the analysis and control of their products.

Gradually the packing establishments began to utilize their own by-products. This required the establishment of chemical laboratories, the first ones being introduced about 1890. By-products were thus responsible for the introduction of chemical laboratories.

Courtesy, Swift and Company.

Fig. 1.—Final Inspection of Dressed Beef.

Courtesy, Swift and Company.

Fig. 2.—Beef Chill. Room 32° to 34° Fahrenheit.

Chilling and Freezing of Beef and Pork

The warm carcasses after slaughter are run at once into the chill room or freezer. The chill room before being filled is held at a temperature varying from 18° to 32° Fahrenheit. As the warm carcasses enter the temperature gradually rises, but an effort is made by the liberal use of refrigerating brine to maintain the temperature at a predetermined figure, which varies somewhat in different houses. The best practice demands that a moderate, continuous, automatic air circulation be maintained during the chilling period. This is to a certain extent self-regulating, provided the cold and warm air ducts from the refrigerating loft are properly designed. The circulation naturally decreases as the animals are chilled. Under the best conditions beef may be chilled sufficiently for shipping purposes in refrigerator cars in 24 hours, but from 48 to 72 hours are generally used for complete chilling, at which time both the beef and coolers have a temperature of from 34° to 36° Fahrenheit.

Hogs are handled in the same manner and the temperatures brought down as rapidly as possible until the fat and flesh are firm enough for cutting. With very effective refrigeration, the chilling of hogs can be accomplished in 24 hours, but in standard practice from 48 to 72 hours are usually required. During chilling there is a shrinkage from loss of moisture—in the case of beef about 2 per cent or less under ideal conditions, and in hogs slightly more than in beef.

It was formerly thought by practical men that a mysterious something, which they called animal heat, must be removed from the animal body by exposure to ordinary room temperature before the carcass could be properly chilled or frozen; that if the animal heat

were not removed prior to chilling or freezing the meat would spoil. Science has shown such ideas to be fallacious, but only in the most recent years has it been possible to change the time-honored customs of the industry by means of physical and chemical proof.

Meat is ordinarily frozen at about 10° Fahrenheit, but may be introduced into a so-called sharp freezer at lower temperature. After it is thoroughly frozen it is stored at a somewhat higher temperature—about 15° Fahrenheit. If a thin section or very small piece of meat is frozen with extreme rapidity, as, for example, by plunging it into brine at any temperature above the cryohydric point, solidification is nearly instantaneous and little change in the physical structure of the muscular tissue occurs. If, on the other hand, meat is frozen more slowly, as in air, under the usual conditions (and this applies particularly to sides of beef or the entire animal in the case of calves, sheep, and hogs), it has been shown by numerous investigations that deep-seated physical changes occur. Lean muscular tissue contains about 75 per cent of moisture, which is associated with the proteins. This water during the freezing process has a tendency to freeze in the form of ice crystals between the muscle bundles, large and small, thus separating and squeezing them. A cross section examined in frozen condition will show larger ice areas than tissue areas, and the slower the freezing process the larger the ice crystals will be. Near the surface, where freezing has been comparatively rapid, the ice crystals and ice areas will be smaller than in the interior where, owing to the slow conduction of heat through the tissue, the freezing process has been comparatively slow. Associated with the ice crystals is a certain proportion of salts and other extractives of the meat. If a piece of frozen meat is thawed rap-

Courtesy, Swift and Company.

Fig. 3.—Standard Cuts of Beef.

idly, there is a loss of meat juice, since complete reversal to the original colloidal condition does not occur. Even when the meat is slowly thawed there is some loss of juice, but less than during rapid thawing. If meat is frozen instantaneously so that the ice crystals do not form in large masses but, on the other hand, are small and intimately associated with the colloidal material, there is practically no loss of meat juice on thawing; but instantaneous freezing is not practical on the large scale.

The chemical laboratories of packinghouses have made many investigations and are constantly called upon for numerous determinations, physical, chemical, and bacteriological, in connection with the chilling and freezing of meats.

Frozen meat in a general sense will keep indefinitely and no bacterial action can occur while it remains in the solid frozen condition, since bacteria can vegetate only in liquid media. It should be noticed, however, that it is the solid condition and not the temperature which inhibits the growth of bacteria. In nutrient media containing brine, bacteria of certain kinds thrive down to the cryohydric point of the sodium chloride-water system; that is, —22° Centigrade (—7.6° Fahrenheit).

When frozen meats are stored for a long period desiccation gradually occurs beginning at the surface and extending into or through the piece. Desiccation is minimized by maintaining the air in a moisture saturated condition, by avoiding air currents, and by closely wrapping or coating the product with an impervious layer to prevent evaporation. Rancidity of the fats also takes place but with extreme slowness and follows more or less the course of desiccation, since it occurs rather more readily after the product

has lost its moisture than before. Enzyme action is not altogether prevented by freezing, the lipase of pancreas continuing active even at low temperatures, but proteolytic enzymes are inactive.

Composition of Meat

In their grosser aspect, meat food products consist of lean meat (proteins), moisture, fat, soluble salts, and bone. Edible organs consist chiefly of proteins, fatty substances, moisture, and salts. Vitamins are present chiefly in the organs and the fat.

The moisture is associated with the lean meat or protein portion and both protein and moisture are present in inverse ratio to the fat. A lean animal contains relatively more protein and water than a fat animal, while a fat animal contains more fatty tissue and relatively less protein and water than a lean one.

Canning and Curing of Meat

The preservation of food products of all sorts by sterilization, followed by enclosure in hermetically sealed containers, was invented by Appert, a Frenchman, in the early part of the nineteenth century. The process came into immediate use and has been practiced from that time to the present, both as a household art and on the largest manufacturing scale. At the present time meat (as well as vegetable products) is preserved in tin-plated sheet iron cans in immense quantities, the procedure being to place the parboiled meat into the tins, which are then capped. A small perforation is left in the top of the tin for the escape of air and steam during the sterilizing process. Sterilizing is accomplished by placing the tins on trays in a

Courtesy, Swift and Company.

Fig. 4.—View in Ham Curing Cellar, 34° to 36° Fahrenheit.

Courtesy, Swift and Company.

Fig. 5.—Preparing Hams for Smoking.

retort in which heat is applied by steam under pressure for a longer or shorter time, depending on the size of the package and the nature of the product. After retorting and while the can is still hot, the perforation is sealed with solder. This comparatively simple but most effective process is based on the fact that both vegetative forms of bacteria and their spores are killed at a temperature somewhat above the boiling point of water and that if recontamination is avoided, particularly by spores and bacteria floating with the dust in the air, the sterilized product will keep indefinitely. Thus it is seen that heat sterilization and the application of cold are two of the most important means utilized in packinghouses for the preservation of a most perishable product.

Salt is the principal chemical preservative used in connection with meat products, although important parts are played by sugar, saltpeter, vinegar, and spices. Salt is applied to hams and bacon in three ways. First, in the dry salting process, it is sprinkled or spread in dry form over the surface of the meat, any juice exuding from the product draining off. Second, the same process is applied to meat, particularly bacon, which is kept in closed containers, thus avoiding the draining of the meat juices, and the salt is gradually absorbed. Third, the hams or bacon are submerged in a brine composed of from 15 to 25 per cent of common salt, 3 to 6 per cent of sugar, and about one-fourth of 1 per cent of saltpeter. A similar mixture of the three curing agents is also used in the dry salting processes.

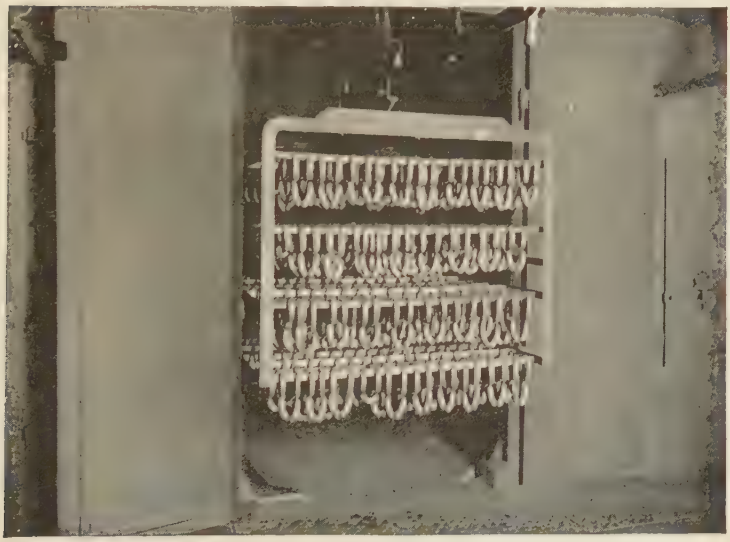
All curing processes take place in coolers maintained at low temperatures, usually 33° to 36° Fahrenheit, since the meat would spoil if the curing agents were applied at higher temperatures. The salt, com-

bined with the low temperature, inhibits the development of bacteria or decomposition; the sugar also assists to a certain extent in this direction but is added mainly as a flavor for the final product; the saltpeter during the curing process is reduced to nitrite, which in turn forms nitrosohemoglobin, which is bright red and maintains the meat in its original red condition. If this procedure were not followed the meat would turn a dull gray owing to the formation of methemoglobin.

Beef hams and beef briskets are corned (cured) in sweet pickle in a manner similar to pork hams, thus producing corned beef. Pork shoulders are similarly cured. In the manufacture of sausage, salt, sugar, saltpeter, and spices (and sometimes a cereal or farinaceous product) are mixed with the ground meat, which is then stuffed into a container or casing made of hog, sheep, or beef intestine. Some sausages, known as summer sausages, are hung in dry rooms until the original moisture content of 65 to 70 per cent is reduced to 30 or 35 per cent. In this dry condition the sausage will keep indefinitely. A variety of hams, known as Italian hams, are pressed to a flattened shape and also dried to a low moisture content. The ordinary ham, shoulder, bacon, or dried beef of commerce, however, is hung in a smoke house and smoked for a period of from 2 to 10 days over a smoldering fire of hardwood. During this process the surface of the meat is dried and impregnated with smoke, which tends to preserve the surface, particularly against mold. To prevent mold and bacterial spoilage it is advisable to store cured products at reasonably low temperature although they will keep for a moderate length of time in any temperature. They are partially and not completely preserved products.

Courtesy, Swift and Company.

Fig. 6.—Chopping Meat for Summer Sausage.



Courtesy, Swift and Company.

Fig. 7.—Sausage Emerging from Smoke House.

Raw materials for curing are regularly analyzed, as are the hams, bacon, sausage, and other products, at all stages of cure. Bacteriological examinations are frequently made. In packing sliced bacon in boxes, the rooms, equipment, and particularly the air, are maintained in a condition free from bacteria and the spores of molds and bacteria. Bacteriological counts are regularly made as a means of control. Investigations of all the processes are constantly in progress to correct and improve them. The losses, which formerly occurred in the curing process and which were of great magnitude, have been practically eliminated by the use of both chemical and bacteriological methods.

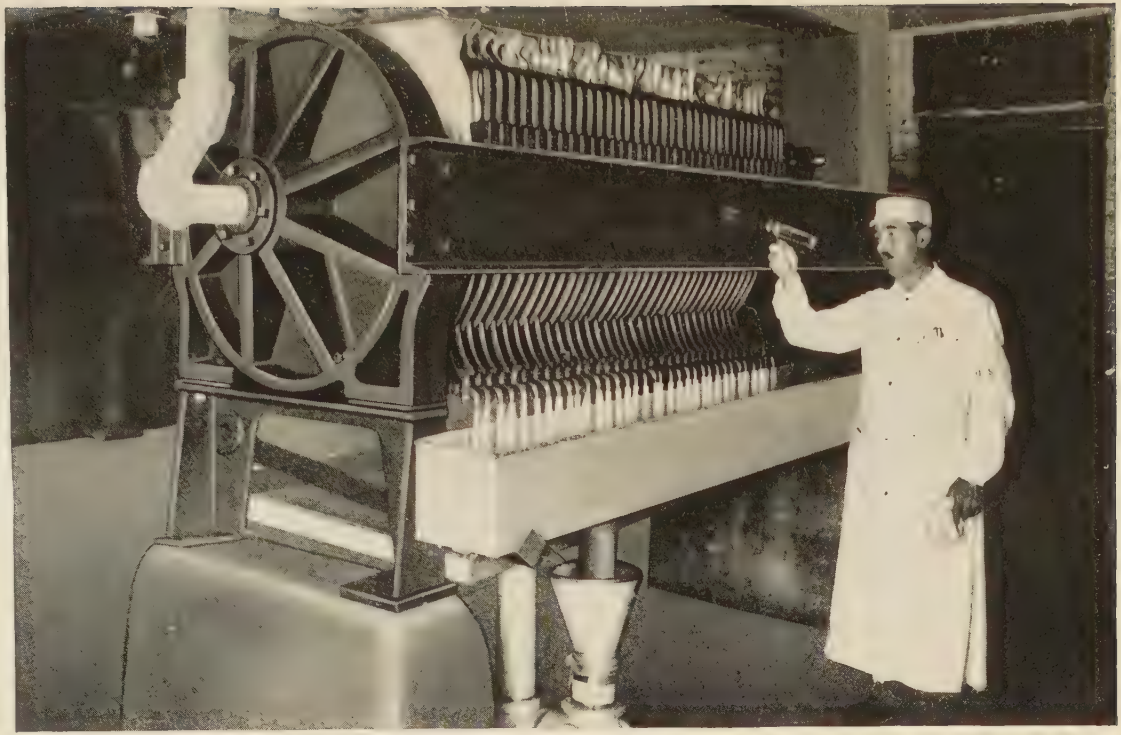
Cattle hides are commonly cured by sprinkling with coarse salt, folding and storing them in a refrigerated room, usually the basement, for a sufficient length of time to allow the salt to penetrate, after which they are shipped to the tannery. In place of this simple procedure they are sometimes washed with water and soaked in saturated brine for about 24 hours, and then dry-salted. This hastens the curing and allows earlier shipment. Sheep skins, after the removal of the wool, are treated with a drench made of bran and water in which lactic acid has been allowed to develop by fermentation, after which they are pickled in a solution containing common salt and a little sulfuric acid. They are shipped to the tannery in the pickled state. Calfskins are salted like cattle skins. Pigskins are salted, frozen, or dried. In packinghouse practice the hog is not skinned.

The only pieces of pigskin obtained are those resulting from the removal of the skin from pieces of back fat by special machines. Sometimes antiseptics other than salt are used to assist in the curing of hides and skins.

Rendering of Fats

Fats and fatty oils, being the so-called glycerides or, as commonly stated, combinations of glycerol and fatty acids (it would be more correct to say compounds which yield on hydrolysis one molecule of glycerol to three molecules of fatty acids), are to be distinguished from hydrocarbon oils (mineral oils) and essential oils, which are for the most part mixtures of hydrocarbons, higher alcohols, and esters.

The distinction between a fat and a fatty oil is merely one of temperature or melting point—a fat being a solid oil, an oil being a liquid fat. Coconut oil is an oil only in the tropics or in warm climates; in the temperate zones it is a fat most of the year. Fats are subject to two principal decompositions: hydrolysis, yielding glycerol and fatty acids of various sorts; and rancidity, which is an oxidation process yielding aldehydes and lower fatty acids of disagreeable odor. The fatty acids occurring in animal and vegetable fats and oils are numerous, belonging principally to three or four series classified according to their degree of hydrogen saturation. It is an interesting fact, however, that all of the fatty acids commonly occurring in natural fats and oils contain an even and not an odd number of carbon atoms. Fatty acids with odd numbers of carbon atoms, although they can be synthesized in the organic laboratory, are of comparatively rare occurrence in organic nature. The saturated or stearic series of fatty acids from acetic, with two carbon atoms, to stearic, with eighteen carbon atoms, are of common occurrence. In the oleic series, with two double bonds, oleic acid is the commonest, being found in animal fats and in nondrying vegetable oils (cf. olive oil). Linoleic acid, with two double bonds



Courtesy, Swift and Company.

Fig. 8.—Filter-Pressing Lard.

and eighteen carbon atoms, is found in the semidrying vegetable oils and in small quantity in lard. Linolenic acid, with three double bonds and eighteen carbon atoms, is characteristic of the drying oils, such as linseed oil. Clupanodonic acid, with four double bonds and eighteen carbon atoms, is characteristic of fish oils.

Thus it is seen that in natural oils or fats, fatty acids with eighteen carbon atoms are most abundant. Coconut oil contains practically the whole series of saturated fatty acids, from two to eighteen carbon atoms (even numbers), although consisting chiefly of those with ten, twelve, and fourteen carbon atoms. The animal oils and fats contain chiefly stearic, palmitic, and oleic acids in varying proportions. The natural glycerides for the most part are not triglycerides, yielding three molecules of the same fatty acid, but are mixed glycerides, yielding different fatty acids, such as distearo-palmitin, dipalmito-stearin, and stearo-palmito-olein, etc. The fatty acid content of various fats and oils has been only imperfectly worked out owing to the difficulty of exact separation of the fatty acids.

Rendering of Lard, Tallows, and Oils

Rendering is a term applied to the melting out of fat from fatty tissue, and in packinghouse practice is accomplished by the following processes:

(1) Low-temperature dry rendering
  (*a*) Neutral lard
  (*b*) Oleo stock and oil

(2) Ordinary dry rendering
  (*a*) Kettle-rendered lard
  (*b*) Dry-rendered lard
  (*c*) Dry-rendered tallow

(3) Steam rendering
  (*a*) Prime steam lard
  (*b*) Tallow and grease

(4) Rendering by heating in the water
  (*a*) Head tallow, mutton tallow, etc.
  (*b*) Neat's-foot oil, etc.

As the fats or glycerides exist in animal tissue they are neutral; that is, they contain no fatty acids; but the means of hydrolysis are at hand since moisture is present and lipase, the fat-splitting enzyme, is very generally distributed through the fatty tissue. Immediately after the death of the animal fatty acids begin to make their appearance, and almost every step in the rendering and after-treatment of fat tends to produce more and more fatty acids. It is the chief aim of rendering processes to prevent hydrolysis and to keep the fatty acid content low. The presence of lipase in fatty tissue can readily be shown by grinding fresh leaf fat (kidney fat) from the hog and incubating it at 38° to 40° Centigrade in the presence of antiseptics to prevent the development of bacteria. Fatty acids increase progressively and readily up to about 40 per cent. During the period when moisture is present in dry rendering and throughout the process of steam rendering, fatty acids are produced, although in small quantity. The lard or oleo stock from kettle-rendering processes usually contains from 0.1 to 0.3 per cent free fatty acids calculated as oleic (which is the custom), while lard from steam rendering usually contains from 0.5 to 0.75 per cent.

The fatty tissue of animals contains from 95 to 65 per cent of fat, the difference consisting of tissue or fiber (chiefly connective tissue) and moisture, the latter being associated with the nitrogenous fiber in the proportion of approximately 4 to 1. Thus, leaf

fat ordinarily contains 95 per cent lard, 4 per cent moisture, and 1 per cent fiber by proximate analysis.

Neutral lard is prepared from the leaf fat (kidney fat) of hogs. The fat is chilled, hashed, and then introduced into the rendering kettles, which are provided with a hot-water jacket and mechanical agitator. The heat is gradually raised and the rendering carried out at temperatures between 120° and 130° Fahrenheit. The residue from kettle-rendering processes is known as "cracklings." These and any residual moisture are allowed to settle, being assisted by scattering a few pounds of fine salt over the surface of the kettle. The rendered lard is siphoned from the kettle by a swivel-joint pipe, strained through fine screening or cheesecloth and allowed to settle again, after which it is placed in tierces to grain (crystallize) in a cooler. Neutral lard is bland in flavor, practically neutral, and is one of the constituents of oleomargarine.

Oleo stock is rendered from the caul fat of the peritoneum of cattle and from the ruffle fat of their intestines. The fats are washed in ice-chilled water, then hashed, and introduced into the rendering kettle, provided with hot-water jacket and agitator. The rendering operations take place at temperatures from 130° to 155° Fahrenheit. After rendering and settling the oleo stock is drawn off into seeding trucks, which are run into rooms maintained at a temperature of 80° to 85° Fahrenheit. Here the stock is allowed to seed or crystallize, the stearin (chiefly a mixture of the natural glycerides of stearin and palmitin) separating from the oleo oil, which is olein mixed with some stearin and palmitin. The seeded mixture of crystalline stearin and fluid oleo oil is folded in cloths and pressed in a knuckle joint press. The oil is squeezed out through the press cloths and thus separated from the hard

stearin. Oleo oil is bright yellow, bland, and a valuable constituent of oleomargarine on account of its high vitamin A content, which on the average is the same as that of butter. Oleostearin is the hardening constituent of lard compound (15 per cent oleostearin, 85 per cent refined cottonseed oil).

Kettle-rendered lard is made from back fat alone, leaf fat alone, or back fat and leaf fat mixed. Heat is furnished to the water jacket by steam under pressure and the temperatures used are moderately high, up to 250° to 260° Fahrenheit. At the maximum temperature used there is a tendency to caramelize the cracklings slightly, thus giving the finished lard a pleasant, cooked odor and flavor. Kettle-rendered lard is practically dry and of excellent keeping quality. It is one of the standard household lards, not being essentially different from that made and used on the farm from ancient times to the present day.

Prime steam lard is made from the fatty tissue trimmed from hams, bacon, shoulders, etc. (cutting lard), and from miscellaneous pieces of fatty tissue from the killing floor (killing lard). The fatty material is introduced into large vertical tanks, about 7 feet in diameter by 14 or 15 feet high, in which it is cooked about 8 hours under 40 pounds steam pressure. After this period, the rendered lard floats on top and is drawn off, settled, and clarified, and bleached with a small amount of fuller's earth. It then becomes the prime steam lard of commerce. The watery layer left in the tank is known as "tank water" and contains gelatin and various nitrogenous extractives. It is drawn off, evaporated in triple effect evaporators (at which stage on account of its sticky condition it is known as "stick"), and mixed with stock feed. The solid residue of tankage left in the tank is dried and

sold either as animal feed or fertilizer, depending upon its grade and quality.

Tallows of various grades are produced from fatty tissue from cattle-killing operations and from the non-edible portions of the animal by the same process which is used for making prime steam lard. Edible tallows are not produced by the steam pressure method as a rule. Lower grades of tallows and also grease (from hog fat) are made from the lower grades of raw material.

There is a tendency at the present time to substitute dry-rendering processes for the steam-rendering processes in order to avoid the expense of handling tank water and tankage to produce higher grades of fat and animal feeds. Dry rendering may be carried out in a horizontal jacketed cylinder containing a horizontal shaft equipped with agitator arms. The fatty material introduced into the cylinder is rendered with slow agitation, the rendered fat drained off, and the residual cracklings pressed in a continuous screw press. By this means only two products are obtained—fat and cracklings, the latter containing about 7 per cent of fat and being of high grade and very well suited for animal feed. Other methods of dry rendering are also in use, some being continuous and others employing vacuum.

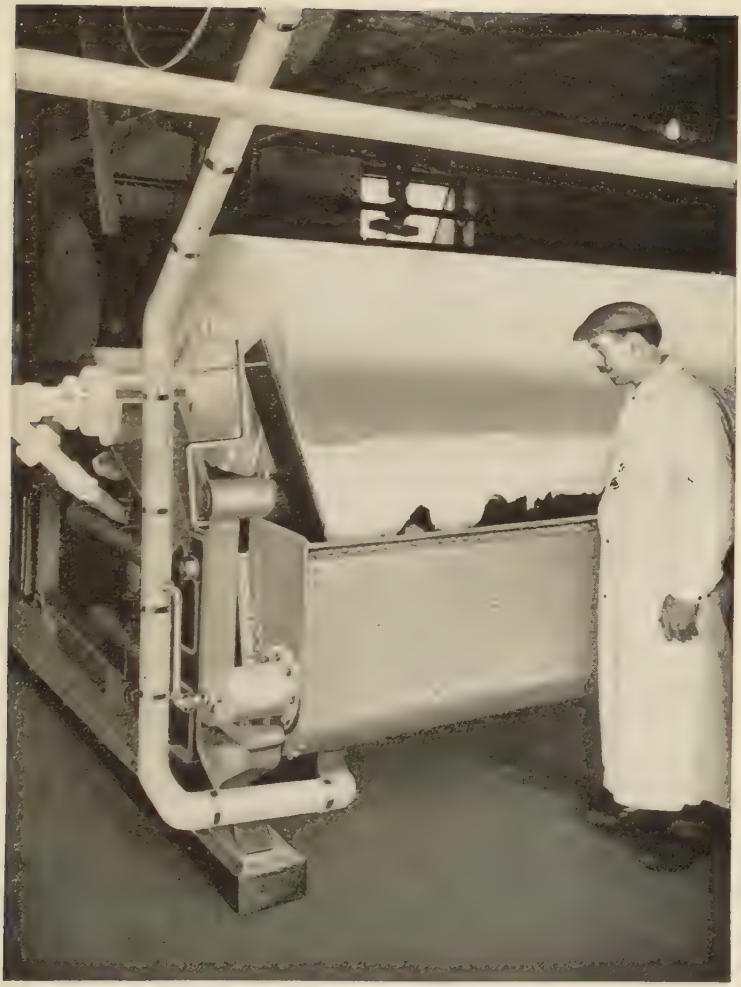
The fat found in heads of animals is usually rendered by boiling in open vats in water. In the same manner neat's-foot oil is rendered from the marrow of shin bones of cattle. Rendering by heating in water is a process which has been applied from time immemorial to various substances such as fish and products thereof, cod livers, meat and bones, palm nuts, etc. The oil or fat is skimmed from the surface from

time to time, then settled, clarified, and refined, if necessary, according to the usual processes.

Chemical and Physical Determinations of Oils and Fats

The determinations most commonly made on commercial samples are: color reading by the Lovibond tintometer, by comparison with standard samples or otherwise; titer—that is, the solidifying point of the fatty acids prepared from a sample of fat; free fatty acid determined by titration with standard alkali and usually calculated to oleic acid; moisture and volatile matter determined by volatilization under prescribed conditions; insoluble impurities; unsaponifiable matter soluble in petroleum ether, commonly called "unsaponifiable matter"; saponification value, being the number of milligrams of caustic potash required to saponify one gram of the fat; iodine number or the percentage of iodine absorbed by unsaturated fats and oils under prescribed conditions; and melting point, which, since fats and oils are mixtures and have no definite melting point, is subdivided into incipient melting point, or softening point, and final melting point. The determinations less commonly made are: specific gravity; acetyl value, which is a measure of the hydroxy group in the fat molecule; and separation of saturated and unsaturated fatty acids by means of the lead-soap method.

Salad oils and animal lubricating oils are examined for cloud test and the latter also for flow test. A considerable number of specific tests are also used to distinguish fats and oils and to detect adulteration—e.g., the Belfield test for the detection of tallow in lard; the Halphen test to detect cottonseed oil or adultera-



Courtesy, Swift and Company.

Fig. 9.—Chilling Lard on Chill-Roll.

tion of other fats and oils therewith; the Valenta test; the Kreis test for rancidity; and the arachidic acid test for peanut oil. The testing of fats and oils is complex and difficult, so much so that it alone, or even branches of it, affords a sufficient field for expert chemists.

Hydrogenation of Fats

Since the difference between soft and hard fats or between oils and fats is due to the double bond of the carbon atom or, expressed in another way, to the unsaturation of the former and the saturation of the latter (hydrogen saturation), it is theoretically possible to complete the saturation of unsaturated oils and thereby harden them by introducing hydrogen into the molecule. This was first accomplished by Normann in 1903 following the work of Sabatier and Senderens. As commonly practiced, the oil to be hydrogenized is introduced into a tank heated by means of a steam pressure coil and provided with an agitator. A catalyst, consisting of very finely divided or colloidal nickel, is added. The hydrogen is recirculated and the entire mass agitated at a temperature considerably above the boiling point of water. Gradually, the hydrogen gas is absorbed and the oil becomes progressively harder, the iodine number at the same time becoming progressively less. The process of hydrogenation is naturally most valuable during periods when oils are comparatively cheap and semisolid fats comparatively expensive. It may be applied to edible and inedible oils.

Refining, Bleaching, and Deodorizing of Oils

The term "refining" is now applied to the oil-treating process, which consists in adding a solution of caus-

tic soda to the oil at a moderate temperature under agitation, whereby fatty acids are neutralized and precipitated as soaps along with various coloring matters and other impurities. Bleaching is accomplished by means of fuller's earth and similar earths with or without the addition of bleaching carbon. Deodorizing consists in blowing saturated or superheated steam through the oil or fat at an elevated temperature, usually under vacuum. Other oil-treating processes are known and used but these three find the widest application. While they are applied most extensively to vegetable oils they are also used to a considerable extent in the treatment of animal oils and fats.

Hydrolysis of Fats

The hydrolysis of fats—that is, the splitting of fats into glycerol and fatty acids by means of the water molecule, or its equivalent—is accomplished in various ways:

1. By means of water alone. This requires the use of high pressures and temperatures as well as agitation to keep the water and fat well mixed.

2. By means of water plus an acid catalyst such as Twitchell's reagent, which is essentially stearosulfonic acid made by treating oleic acid with concentrated sulfuric acid. The process is carried out by boiling in open wooden vats by means of steam.

3. By means of an alkaline catalyst, usually calcium or magnesium soap. Calcium oxide or magnesium oxide or both are introduced into an autoclave and heated with steam under pressure. The oxides saponify a portion of the fat, forming the corresponding soaps, which then act as emulsifying catalysts.

4. By means of enzymes. These are found generally distributed in fatty tissue, both animal and vegetable. The

lipase of castor oil bean and of the pancreas are especially well known. With these, hydrolysis may take place at ordinary temperatures, but the splitting seldom goes beyond 70 or 80 per cent.

5. By means of caustic alkalies, as in the ordinary process of soap manufacture. In this process, while glycerol is produced on the one hand, the corresponding fatty acid combines at once with the caustic soda or caustic potash used to form sodium or potassium soap. Ordinary soaps are hard soaps or sodium soaps; potassium soaps are made less frequently and are soft soaps, such as the green soap used by surgeons.

The primary purpose of the hydrolysis of fats by the autoclave or the Twitchell process is the production of glycerol and fatty acids. The fatty acids are crystallized or seeded and pressed, thus producing both commercial stearic acid and oleic acid or red oil. Candles are made from commercial stearic acid or a mixture of this with petroleum paraffin; red oil is used for the manufacture of soap.

Rancidity

Although there is much confusion in the literature on the subject, rancidity is a purely chemical process in which bacteria are not involved, and it is important that it should be recognized as such. Because bacteria sometimes produce bad-smelling lower fatty acids in emulsions of fats, bacterial processes, chiefly hydrolytic, have been confused with rancidity, which is essentially a chemical oxidation process. Although rancidity occurs in fats apparently free of moisture, a minimal amount of moisture appears to be necessary to its development; probably the moisture in the air furnishes a sufficient amount. It occurs in commercially dry fats of all sorts and under all conditions,

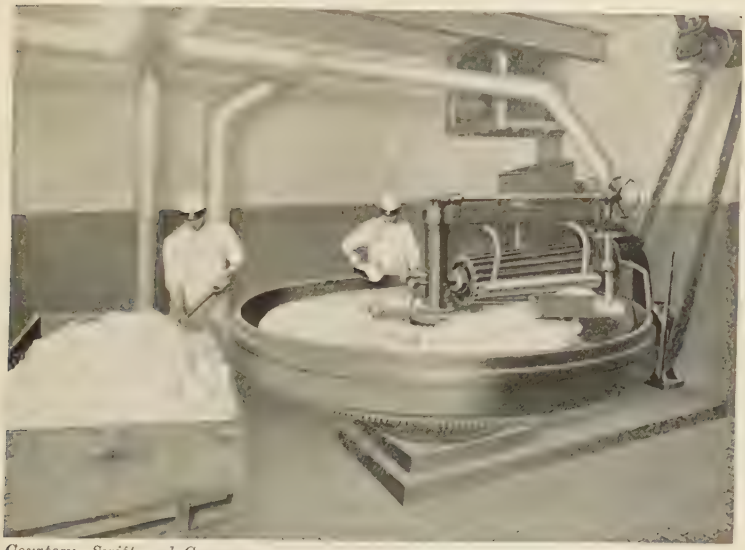
even in the dark and at low temperatures. The presence of air is the first necessity and the process is enormously accelerated by the ultra-violet rays of sunlight. It is accelerated also by the presence of catalytic metals, the most important of which from the practical standpoint are copper and iron. Therefore, fats should never under any circumstances be brought in contact with copper or with rusty iron. They can be handled in clean iron kettles with comparative safety, although contact with metals of any sort promotes rancidity in varying degree, copper being extremely active and aluminium only slightly so. The metals or metallic oxides dissolve in the fats to form metallic soaps or compounds of metals and fatty acids—the active catalysts of rancidity. Inhibiting catalysts or negative catalysts of an organic nature are also known. Unsaturated fats and fatty acids seem most prone to rancidity but the saturated ones are by no means exempt.

The products of rancidity are largely lower fatty acids and aldehydes of extremely repulsive odor. Specific chemical tests for these products of rancidity are not known, but use is made of general reagents for aldehydes and, particularly in recent years, of the Kreis reagent (phloroglucinol anl hydrochloric acid) for their detection. Organoleptic tests are the best and most positive, except for incipient rancidity, since the Kreis test is sometimes given by nonrancid oils, which have, for example, been overheated.

During the course of rancidity the volatile products formed may volatilize, thus balancing (or overbalancing) the gain in weight caused by oxidation. In shallow dishes, exposed to warm sunlight, fats lose weight rapidly and may eventually diminish to 40 per cent or more of their original weight.

Courtesy, Swift and Company.

Fig. 10.—Oleomargarine Emulsifier.



Courtesy, Swift and Company.

Fig. 11.—Oleomargarine Worker.

Oleomargarine

Oleomargarine consists of a mixture of fats of semisolid consistency at ordinary temperatures churned with milk which has been ripened by means of a lactic acid ferment similar to that used for butter. It is the invention of Hippolyte Mége, who, in 1869, developed the method of manufacture at the Royal Farm at Vincennes, France, for which he received the prize offered by Napoleon III for a substitute for butter which should be cheaper than butter, keep better, and be less liable to rancidity. The margarine of Mége was an oleo oil product, whereas modern margarine consists of a mixture of animal and vegetable fats and, in some cases, of vegetable fats alone.

A typical oleomargarine is made of a mixture of oleo oil, neutral lard, and refined cottonseed oil in suitable proportions to make the semisolid product demanded by the trade. The mixture of oils and fats is introduced into the churn or mixer, together with the ripened milk, and emulsified. The emulsified product is chilled to solid condition, either by running it into ice cold water and thereby crystallizing it, or by running it upon the surface of a revolving steel drum or roll whose interior is chilled by cold water or brine. The chilled product is taken off by means of a knife edge. However the chilling is performed, the product is placed in trucks, salted, worked, and molded into tubs or prints. A typical vegetable margarine is made of refined coconut oil which may have added to it, in hot weather, a little stearin or hydrogenized peanut oil in order to raise its melting point somewhat. The manufacturing methods are similar to those used for oleomargarine.

Manufacture of Gelatin

The white fibers of connective tissue when boiled with water first swell and then dissolve to form gelatin, a typical colloid and the starting point of Graham's classical researches on this subject. Chemically, the white fibers are known as collagen. Collagen is very generally distributed in animal tissue, particularly in the skin, the bones, and fatty tissue, and the first two of these are the commercial sources of the product. Collagen is probably not a single chemical substance but represents a group of closely related substances of slightly differing properties. The skins of young animals form gelatin upon boiling much more readily than the skins of old animals. Any gelatin on continued boiling with water or heating with water under pressure, especially in the presence of acids or alkalies, becomes hydrolyzed, loses its gelatinizing power, and ultimately breaks down into amino acids. These facts, together with other evidence, lead to the assumption that there are several related products in the collagen-gelatin series, which may be roughly grouped for convenience as follows: old collagen, young collagen, disperse collagen, true gelatin or alpha-gelatin, hydrolyzed gelatin (also called beta-gelatin or gelatone), and amino acids. Ordinary edible gelatin consists chiefly of true gelatin but may contain varying quantities of other substances, particularly beta-gelatin.

All commercial gelatin is classified according to its source as bone gelatin or hide gelatin, and the methods of preparation vary with the raw material.

Hide gelatin is made from calfskin, pigskin, and trimmings from other skins and hides. The pieces of skin are first treated for a considerable period with milk of lime in liming vats. They are then thoroughly

washed in a mechanical washer in running water and taken to the cooking kettles in which several cookings are made. The first liquors are taken off at a low temperature—as low as 130° or 140° Fahrenheit. These produce the best and strongest gelatin. Successive runs are taken off at increasing temperatures until seven or eight cookings have been made. Some of the runs are combined and all of the liquors evaporated in a vacuum evaporator, avoiding any undue temperature or period of heating which would weaken the product by hydrolyzing it to beta-gelatin. The concentrated liquors are allowed to set to a jelly in pans in a chill room or in sheets upon a rubber belt in a continuous chilling machine. The pan-chilled gelatin jelly is next sliced by hand and the sheets spread upon wire nets in a drying tunnel, through which a strong blast of dust-free air, carefully regulated as to temperature and humidity, is blown. The machine-chilled sheets are spread and dried in the same manner to a moisture content of 8 or 9 per cent for convenience in crushing and grinding. Upon storage the moisture content usually rises to 11 or 12 per cent under ordinary atmospheric conditions. Gelatin is sometimes dried upon the surface of a drying roll or wheel in a continuous manner.

Bone gelatin is made from the clean bones derived from the heads and feet of cattle, sheep, and hogs in packinghouse operations. These are first boiled for a longer or shorter time to remove fat, which is skimmed from the cooking vats. After the bones are crushed, gelatin may be obtained from them by boiling in an open vat (poor yields) or cooking in steam pressure tanks (better yields), but the usual procedure is first to manufacture ossein from the bones. Ossein is the trade name given to the collagen material left after

removal of mineral matter (calcium phosphate) from bones by means of hydrochloric acid. The steps in ossein manufacture are: (1) cooking to remove loose tissue and some of the fat or oil; (2) drying and crushing the bones; (3) extraction of the fat by means of a volatile solvent; (4) a second crushing and sizing of the crushed bones; (5) soaking the crushed and sized pieces in hydrochloric acid, from 2 to 5 per cent strength, in order to dissolve calcium phosphate; (6) washing the ossein to remove acid, and if it is to be stored, drying it. The acid-soaking operation is conducted in wooden vats and the strength of acid and also the time of soaking are varied according to the size of the crushed bone treated and the temperature. Ossein is cooked in vats in a manner similar to hides and skins. Ossein gelatin is an excellent product, light in color and of high strength. Bone and ossein gelatin liquors are concentrated, chilled, and dried according to the same methods as hide gelatin liquors.

The finished gelatin, whether hide or bone, is graded chiefly on the basis of its jelly strength, which is carefully determined in the laboratory by means of an apparatus known as the gelometer.

From first to last, gelatin manufacture is under strict chemical, physical, and bacteriological control. The bacterial count in the finished product must be low. Government regulations limit the permissible amounts of metals, such as copper, zinc, and arsenic, which may be present, and hence all operations are conducted in apparatus made of wood or noncorrodible metals, such as aluminium and monel metal. There are special specifications for gelatin which is used for preparing the photographic emulsion on dry plates and films, for making capsules, for marshmallow and candy manu-

facture, and for use in ice cream, as well as for the ordinary table use in jellies.

Although gelatin is a valuable food product it is not a complete protein in the sense of the proteins of meat, eggs, and milk, but is as complete as many of the vegetable proteins. The term "complete protein" is understood to mean a protein which contains all of the amino acids required for the nourishment of the human body.

The following determinations are commonly made upon gelatin samples, either for the purpose of grading and meeting specifications or for factory control: moisture, jelly strength, viscosity, pH value, bacteria count, ash, metallic impurities such as copper, zinc, and arsenic, and foam ability.

Manufacture of Glue

The same raw materials which are used in gelatin manufacture are also used for the manufacture of glue. However, since glue is an inedible product the same care in the selection of raw materials and in manufacture is not required. The old idea that glue is made from hoofs and horns is one of those notions which persist in spite of continued denial and reiteration of the facts. Hoofs and horns belong to the group of keratins, which are complex proteins entirely distinct from the collagen of the white fibers, and do not yield gelatin on boiling. Hides and skins are subjected to the same preliminary treatment for glue as for gelatin. Bone glue is made either from green bones (green bone glue) or dry bones (dry bone glue), but the acid process (ossein process) is not used for glue manufacture ordinarily, as it is too expensive. Bone glue is made in pressure tanks, successive runs of liquor being

taken off until the last runs are too weak to save. Weak glue of this sort is used for sizing. The operations of concentration, chilling the liquors to a jelly, drying, and grinding are similar to those described for gelatin. The majority of glues are sold in granular condition (ground) and are blended from different runs to insure uniformity of grades and to meet definite specifications. Various additions to glues are made during the process of manufacture—formaldehyde to prevent decomposition, zinc oxide and zinc sulfate as preservatives and in opaque glues.

The principal chemical and physical determinations made on glue samples are: jelly strength by means of the gelometer; viscosity by the viscosity pipet; reaction (pH value); grease content (the grease should be as low as possible); and foam determination.

Research for the improvement of processes of glue manufacture is always in progress.

Glands and Organotherapeutic Products

The glands of the animal body are divided into two groups. One group is provided with ducts and their secretions are poured out through these ducts into the gastrointestinal canal or elsewhere for purposes of digestion; such, for example, are the salivary glands, the pancreatic gland, and others. To the second group belong the ductless glands, or endocrines, whose secretion is poured directly into the blood stream. The secretion of the ductless glands consists of hormones, or chemical messengers, which circulate in the blood stream and exert control over various parts and functions of the body. The following are the more important of these glands: the suprarenal, which yields adrenalin, largely used in surgery and for other purposes; the pituitary,

Courtesy, Swift and Company.

Fig. 12.—Analyzing Fertilizers.

yielding pituitrin; the isles of Langerhans in the pancreas, yielding insulin, used in the treatment of diabetes mellitus; the ovary, yielding ovary extract and corpus luteum; the thyroid gland, used in desiccated form and also in extract form (thyroxin, discovered by Kendall, is the active principle or one of them); thymus gland; pineal gland; and the testes.

Gland therapy is in its infancy and only the first steps have been taken in the investigation of gland extracts and hormones, their preparation in pure form and their demonstration in disease.

The digestive ferments—pepsin from pigs' stomachs, pancreatin from pancreas, and rennet from calves' stomachs—are usually manufactured in the gland department.

Organization and Operation of the Packinghouse Laboratory

The laboratory has two main branches, the analytical laboratory and the research laboratory, whose functions sometimes overlap and whose men are sometimes transferred. The analytical laboratory has the following divisions:

1. Meat and meat products; curing materials; ham, sausage, bacon.
2. Fats and oils; lard, tallow, coconut oil, cottonseed oil; raw materials for margarine; raw materials for soap.
3. Soap and glycerol; fats and oils; caustic soda and soda ash; fatty acids and cottonseed foots; essential oils; soap in process, finished soap, competitors' soaps; glycerol lyes, dynamite, and C. P. glycerol.

4. Gelatin and glue; chemical and physical testing of raw materials, intermediates, and finished product.
5. Fertilizers; dried blood, tankage, and steam bone, raw materials of and mixed commercial fertilizers; potash salts, sulfate of ammonia, nitrate of soda, phosphate rock, acid phosphate, etc.
6. Animal feeds; dried blood, meat scrap, digester tankage, cracklings, mineral salts.
7. Engineering supplies; coal, water, metals, paints, Portland cement; roofing, insulation, paper; etc.
8. General supplies; salt, sugar, saltpeter; vinegar, spices, etc.

The research laboratory is divided into the same departments, in a general way, as the analytical laboratory, corresponding to the principal operating departments of the plant; less attention is given to supplies and more to animal glands, gelatin, glue, soap, oils and fats, margarine and lard, nutrition and bacteriology.

The large establishments maintain fifteen or twenty branch laboratories, in branch packinghouses, fertilizer works, soap works, gelatin plants, and others; and as many as fifty or sixty smaller test laboratories are kept in operation for making some of the simpler routine determinations and tests for the control of product.

Chart 3 shows in schematic form a typical packinghouse laboratory organization.

Past and Future of Science in the Packing Industry

Although science entered the packing industry somewhat late in its history, it was nevertheless at a critical period in its development, when mechanical refrigeration was taking the place of natural ice refrigeration, and mechanical devices, the place of hand labor. Thus, the chemist, physicist, and bacteriologist could work hand in hand with the construction engineer and mechanical engineer. During the last decade of the nineteenth century many of the managers of the business thought that their goal had been reached, that all by-products had been saved, and that all operations were carried out in the best manner possible. This idea was a natural one, because of the enormous development of the industry from its simple foundations. It should be borne in mind that the packing industry as developed in America is distinctly a new industry and received no guidance from the Old World. Nearly all other industries have been transplantations. The advent of science brought in improved practices in every direction. In fact, the industry underwent a new development, and this development is still in progress; indeed, at the present moment it may be said to be at its height. Perhaps the greatest contribution of science may be summarized in the statement that a certain reasonableness has been introduced into all operations and the bad practices, fads, prejudices, and notions which formerly grew up and had equal standing with very excellent and logical methods have been nearly all eliminated. Science has permeated every department of the business and it may be said that there are no departments in which scientific methods and results have not been applied.

CHAPTER XV

CHEMISTRY IN THE PULP AND PAPER INDUSTRY

MAXIMILIAN A. KRIMMEL
Hammermill Paper Company

When chemistry introduced wood into the paper industry as a raw material for pulp or fiber, it was probably the greatest contribution of this science to an industry which is the seventh largest in the country. In order to appreciate fully the significance of this contribution, it is necessary to know something about the development of pulp and paper manufacturing up to the time when wood was utilized; also to have a general idea of how paper is made.

Paper consists essentially of a large number of small, hair-like fibers, matted and interwoven so closely that they form a continuous surface. Some conception of the size of these fibers can be formed by tearing a sheet of paper and examining the torn edges. The small, hair-like particles projecting from the edges are the fibers which form the basic constituent of all papers. In a sheet of paper the size of the leaves of this book there are about two million fibers of natural length, but actually six million fragments of fibers.

These fibers must first be extracted from the state in which they occur in nature by one of the so-called pulping processes; and because of the appearance of the mass of fiber at this stage of the process, it is

often referred to as pulp. This fiber, or pulp, is then washed, screened, and given special chemical treatment, depending upon the kind of paper desired. After this preparation it is mixed or diluted with a large volume of water. The mixture contains one part of fiber to one hundred and sometimes two hundred parts of water. In this very dilute state the fibers pass on to the first part of the paper machine—an endless moving wire screen. Here the water falls through the meshes of the screen and the fibers remain on it matted into a web by the motion of the screen. It is here that the paper is formed, but before it can be used as such, more water must be removed. This is accomplished by conducting the wet web of fiber through press rolls and then over steam-heated cylinders. Individual fibers mixed with water are fed into one end of the machine and are removed at the other end in a continuous sheet of dry paper.

Paper can be made today by the same methods employed by the ancient paper makers of China. Then it was all made by hand with few materials and very little equipment. In fact, all that is necessary is some fibrous substance, water, some stones or other implements for pounding the raw material, a screen made of metal or silk, and ordinary skill. To make paper under these conditions, one would take material such as pineapple stems, soften them and separate the fibers as much as possible, then reduce the fibers to shorter length by pounding them between stones, and, after being thus cut up, the mass of fibers would be mixed with water in a large container. Into this container the screen would be dipped and shaken as removed. The fibers would form a web on the screen as the water passes through the openings and when dry it could be used as paper.

The paper made in this fashion would hardly be suitable for the uses to which paper is put today. On the other hand, an excellent grade of paper can be made by hand, with the proper selection of fibrous material and a few refinements in the crude primitive process just described. In fact, some of the very artistic papers of today are still made by hand, but the quantity that could thus be made would be far from sufficient to meet the demand. It is indeed fortunate that we do not have to depend upon such a source for our present supply of paper. We would be handicapped still more if we were forced to rely upon the amount made in the early Egyptian fashion, of laying fibers of the papyrus reed crisscross upon each other to form a sheet. Chemistry was not applied in any of these primitive processes of paper making except that lye, extracted from wood ashes, was sometimes used to make the softening of the fiber less difficult.

Fibers suitable for making paper can be secured from several sources. They are found in all plants and are as widely distributed in the vegetable kingdom as iron is in the mineral world, but they do not occur the same way in the various plants. In the cotton plant these fibers are the hair of the seed and are therefore the cotton fibers. In plants like flax, the fibers are found in the inner bark and are known as bast fibers. Linen consists of the bast fibers of the flax plant. In other plants like straw, esparto, bamboo, and cornstalks, the fibers are present in the entire stems. In trees they are cells of the woody portion. Therefore, different methods must be applied to obtain the fiber.

The early history of paper making is so obscure that it is impossible to say definitely how soon chemical

methods were applied to separate the fiber from its natural surroundings. Certainly it can be presumed that when chemistry was introduced the preparation of the fiber for the sheet making became less laborious, quality was improved, and production increased. Early in the nineteenth century handmade paper was almost completely eliminated by the invention of the paper machine. Development of this equipment naturally resulted in a means of converting large quantities of fiber into paper and placed paper within the reach of a greater number of people. Up to this time most paper was made from linen and cotton rags—linen and cotton fibers find their most important use in the textile industry for the manufacture of cloth. Therefore, the paper makers of this period really depended upon the product of another industry for their raw material. As the demand for paper was increasing, it soon became very evident that rags as a source of supply for fibrous matter would shortly be inadequate.

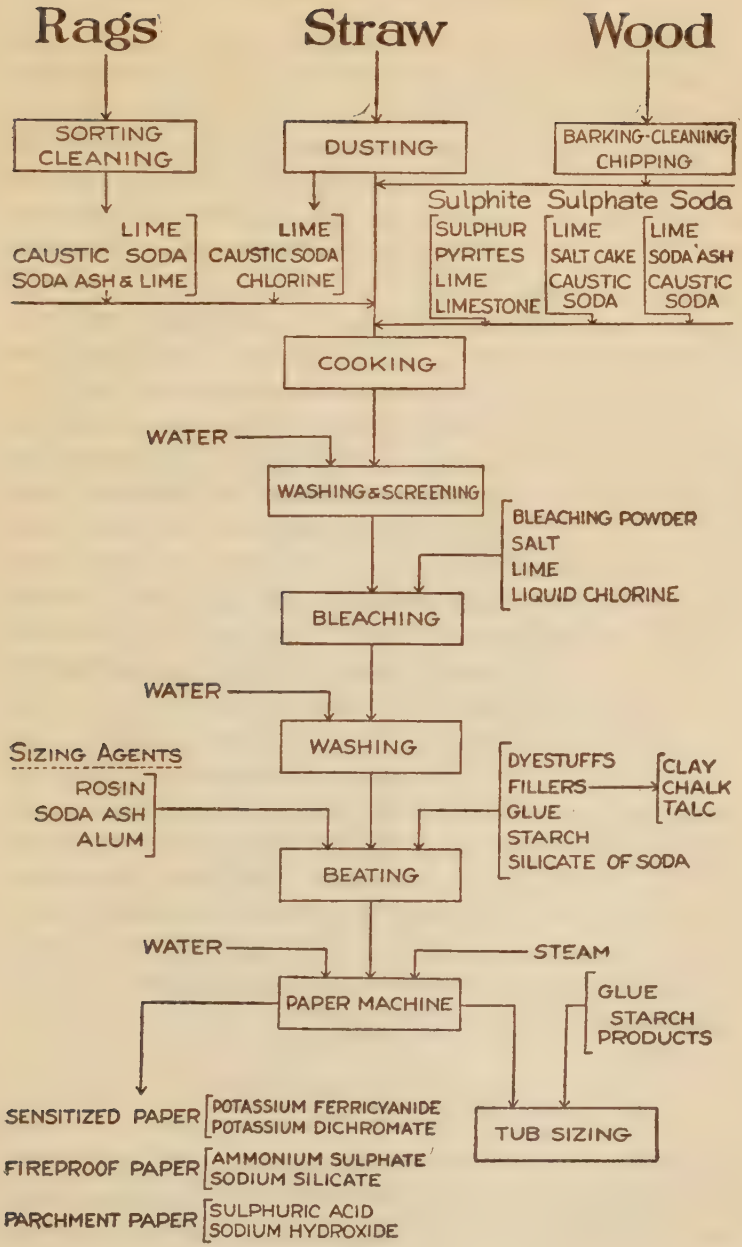
First Use of Wood

In the middle of the nineteenth century when wood was introduced as a source of supply of fibers for paper making, an enormous quantity of fiber was made available. This discovery came at a time when the paper machine was being rapidly developed to make a product in quantities large enough to meet the ever increasing demand. Great progress was being made in other lines of industry through a more general exchange of ideas with the wider use of paper. Therefore, this one contribution of chemistry played a singular role, not only in the development of the paper industry, but also in the expansion of other industries, and greater still in the progress of civilization. Paper,

which was at one time known only to those skilled enough to make it or wealthy enough to buy it, was made available to all through chemistry. The fact that most papers made today contain wood fiber is further proof of the important part this class of fiber plays in the industry. Prior to the recovery of cellulose fiber from trees, wood had been used as a source of supply of pulp which, from its character, was destined to have a limited although important use. In the ground-wood process, a log from which the bark has been removed is pressed against the outer surface of a cylindrical-shaped stone revolving in water. Resulting from this treatment is a pulp consisting of minute particles of all portions of the wood—fibrous and nonfibrous. It happens, however, that this latter constituent deteriorates when in contact with air, and thus paper made from this pulp lacks permanent qualities and cannot be used where strength and durability are desired. Obviously, it could not replace rag-fiber pulp even to the slightest extent. Ground-wood pulp is used to make newspaper and cheap wall board, but even when employed in this manner it must be mixed with stronger and more durable fibers in order to yield a satisfactory product for the trade.

From raw material to the paper machine, the manufacture of paper is a chemical process. It is more complicated where such materials as wood, straw, or grass are used than in mills where rags are used as the source of the fiber.

In the case of pulp made by the ground-wood process there is little chemistry involved and the product is known as mechanical pulp. All fibers resulting from any other process except from rags are known as chemical pulps and are named according to the particular chemical employed. The accompanying diagram,


Rags
Straw
Wood
SORTING CLEANING
DUSTING
BARKING-CLEANING CHIPPING
LIME
CAUSTIC SODA
SODA ASH & LIME
LIME
CAUSTIC SODA
CHLORINE
Sulphite Sulphate Soda
SULPHUR
PYRITES
LIME
LIMESTONE
LIME
SALT CAKE
CAUSTIC SODA
LIME
SODA ASH
CAUSTIC SODA
COOKING
WATER
WASHING & SCREENING
BLEACHING POWDER
SALT
LIME
LIQUID CHLORINE
BLEACHING
WATER
WASHING
SIZING AGENTS
ROSIN
SODA ASH
ALUM
DYESTUFFS
FILLERS
GLUE
STARCH
SILICATE OF SODA
CLAY
CHALK
TALC
BEATING
WATER
STEAM
PAPER MACHINE
GLUE
STARCH PRODUCTS
SENSITIZED PAPER
POTASSIUM FERRICYANIDE
POTASSIUM DICHROMATE
FIREPROOF PAPER
AMMONIUM SULPHATE
SODIUM SILICATE
PARCHMENT PAPER
SULPHURIC ACID
SODIUM HYDROXIDE
TUB SIZING

page 241, shows the various chemicals used in the different processes and in the stages of pulp and paper manufacture. Reference to it should be of assistance in studying the part which these materials play in the paper industry. It also shows fiber sources, conversion processes, and the principal stages in the preparation of the fiber for the machine, viz., cooking, bleaching, and refining.

Fibers consist principally of a highly resistant substance called cellulose. The forms of cellulose are varied but it always consists of the same chemical elements—carbon, hydrogen, and oxygen—in a definite proportion. In the fiber of the cotton plant we find the purest form of cellulose. But no matter what is used as a source of cellulose fiber, chemical treatment is necessary in the so-called "cooking" to secure a sufficiently pure fiber for paper making. Rags, straw, esparto, and materials of this class require less treatment than wood, and in each case the method varies with the grade of paper in which the fiber is to be used. Rags are boiled with lime or caustic soda alone or in a mixture of both. In so doing, the starch used in the textile industries, and any grease, or other foreign matter, are eliminated. Straw is given a variety of treatments, from a quick "cook" with lime to produce pulp for cheap straw boards, to a more thorough boiling with caustic soda, or treatment with chlorine, more completely to remove the noncellulose substances and to produce a higher grade fiber.

From Wood to Fiber

Three methods are used to secure fiber from trees, depending upon the kind of wood and on the intended use of the fiber. In the most widely used—the sulfite

process—spruce, balsam, and hemlock-barked logs, after being reduced to chips, are cooked with a solution containing lime and sulfur in a combination known as calcium bisulfite in which there is a certain quantity of sulfur dioxide gas which plays a very important part in the process. Fiber so made is called sulfite pulp. In the soda process, poplar and woods of this class are digested with caustic soda solution which is an alkali—directly contrary to the sulfite process in which the cooking liquor is an acid. This fiber is known as soda pulp. Sulfate pulp is made by the sulfate process, which is really a modification of the soda process. The cooking liquor is a mixture of caustic soda and sodium sulfide—the name "sulfate" being derived from the addition of sodium sulfate at a certain stage of the process. Wood, such as southern pine and other very resinous wood, is utilized in this process. Generally speaking, wood needs longer cooking than the other materials, but in all processes the reaction is carried on under pressure and at temperatures varying with the results to be attained.

The high resistance of cellulose is used as a basis for all of these preparatory measures. The chemicals used dissolve the noncellulose constituents, freeing the fibrous cellulose. There is a limit to the resistance of the cellulose, however, so that if the chemical reaction of cooking is carried too far, the cellulose fiber is attacked and an inferior grade of fiber results, as well as a lower yield. With these facts and the general procedure of the various cooking processes in mind, it becomes evident that chemistry plays a very important part in this branch of the paper industry.

The preparation of the acid and alkaline solutions for these processes requires chemical plants of considerable size. For example, in soda mills the alkaline

liquor, after it has dissolved all the noncellulose portion of the wood, is concentrated and then burned. Alkaline compounds are extracted from the ash and used again for another "cook." The object of the procedure is to economize on materials used and the nonfibrous portion acts as fuel to accomplish this. It requires an acid plant to make the cooking liquor for the sulfite process. Sulfur in native form, or pyrites (a compound of iron and sulfur), must be burned to form gas, sulfur dioxide, which is passed through lime solution or over limestone. Chemistry is involved in the manufacture of both of these products.

The most common solvent known—water—is used freely and in great quantities in the next stage of the pulp process. The material dissolved from wood must be completely separated from the fiber. This is done by washing the fiber with water. Then additional water is used to facilitate the screening process where fiber is separated from knots, uncooked wood, and any foreign matter.

It is impossible to remove all of the incrusting organic material from the fiber in the cooking process without destroying its strength. Nor can this be accomplished in the subsequent washing process. Therefore, to purify the fibers completely, these last traces of organic matter are eliminated by bleaching—again a chemical process in which calcium hypochlorite solution reacts with the water present to liberate oxygen, which combines with the fiber impurities to form compounds which can be eliminated by washing. As in the case of liquors for the cooking process, the bleaching solution necessitates a chemical plant for its preparation.

Refining Processes

In the refining process the fibers are beaten, dyed, sized, and specially treated for the purpose of fitting them for the particular grade of paper in which they are to be used. Before any fiber can be converted into paper it must be beaten to reduce the fibers to a uniform size, the ends split, and the edges softened to promote matting on the wire of the machine. While at the present time this is accomplished mechanically in tubs called beaters, it can also be effected chemically.

If a colored product is wanted, dyestuffs are added. As a great variety of colored paper is on the market, it takes no great amount of imagination to picture the number of different dyestuffs used. A mere mention of the word "dyestuffs" is sufficient to remind the majority of readers of the amount of chemistry called upon in their preparation. In the paper mill, chemistry assists in the proper selection of dyestuffs, taking into consideration the pulp at hand, and paper desired.

Various chemicals, such as starch, glue, rosin, alum, silicates of aluminium and magnesium, calcium sulfate, calcium carbonate, and others are added to produce different characteristics in the finished paper. It is needless to say that the reactions of these compounds with the pulp and other ingredients must be understood if good results are to be attained.

The most important process which goes on with the beating is sizing. It is here that the fiber is made resistant to ink so that the paper can be written upon without the ink spreading as it does on newspaper. This is, of course, an essential quality of writing paper although not for newspaper. It is secured by coating

the fibers with resinous matter in a rather complicated manner. Rosin left as a residue after the distillation of turpentine from crude rosin is melted, treated with alkali, blown into minute particles, mixed with water, and passed into the beater with the pulp. It requires the addition of alum to convert the rosin into a form which will cover the fibers and fill the spaces between them.

Processes described thus far pertain principally to the manufacture of writing, book, and wrapping papers, and newspapers. In the making of specialties such as parchment paper, moisture-proof, fireproof, insulating, roofing, waxed, coated, and safety papers, the qualities which give these grades their names are imparted to the fiber while in the beater or to the finished paper. In all of these special processes chemistry is called upon wholly or in a large measure to accomplish the result.

Function of Water in Paper Making

Water, which has been mentioned briefly in connection with the washing process, plays a prominent part in the paper industry. It enters into all phases of the process, but its two main functions are washing and conveying. In mills where high-grade papers are made it is essential that the water be clean, colorless, and free from dissolved compounds which would interfere with the many chemical reactions throughout the process. An enormous quantity is necessary. For instance, a mill making 130 tons of pulp and paper in 24 hours uses twenty million gallons of water in that time, which is almost as much as the amount consumed by an industrial city of 125,000 population. In the majority of plants all water used in the process must be

filtered, and in many cases chemically treated before filtration, to secure a crystal clear water. A great deal of steam is needed in the cooking process and in the steam-heated cylinders on the paper machines to dry the paper. Naturally, a large quantity of water must be evaporated to provide steam. If the water is hard it contains substances in solution which will deposit as a scale on the evaporating surfaces of the boiler, resulting in a larger consumption of coal because heat from the burning coal cannot be transmitted through this deposit as well as through iron of the boiler. Chemical treatment of water before use in the boilers eliminates the scale-forming compounds with a consequent reduction in coal consumption and increase in the life of the boiler.

Hand in hand with chemistry, engineering has played an important part in the development of the paper industry. Paper is actually made on the paper machine, and the modern machine is one of the biggest contributions of engineering to this industry. It is all the more appreciated when we recall that only about 200 sheets of high-grade paper or 1200 of lower grade could be made per day by one man, while today paper machines 100 to 240 inches wide make paper continuously at the rate of 400 feet per minute of the former and 1000 feet per minute and over of the latter. But without detracting a particle from the important role of the paper machine, it can be said that chemistry controls the quality of the product fed to the paper machines and upon it depends the quality of the finished paper, no matter how perfect mechanically the paper machine is.

A modern paper mill in which pulp is made by one or several of the chemical processes, really consists of a group of auxiliary chemical plants, each produc-

ing a chemical product which is used in the main process, and which influences the quality of the finished products, pulp and paper. Chemistry has developed these auxiliary plants to a stage where it is now possible to determine the exact relation of the auxiliary product to the main product. Briefly, chemistry has brought about better quality, greater production, and more economical use of materials.

Our Paper Age

Perhaps the importance of paper to us as individuals and as a nation can best be emphasized by trying to picture the confusion and discomfort that would exist if we should suddenly substitute stone for paper or in same way suddenly and completely eliminate paper from our daily lives. We have a slight means of judging the stone substitution, for history tells us that this material was used for records and as a means of communication. One can get a fairly good idea of how much business was conducted by correspondence in this manner by observing the modern methods of writing on tombstones. It is safe to say that there would be no vestpocket editions of any books and the records of a modern office building would look like a veritable pile of stone.

But one with the most vivid imagination could not properly describe a paperless condition. Paper is such a common commodity in our daily life that it would be difficult indeed to find a suitable substitute in sufficient quantities. Almost everyone is familiar with the most common uses of paper and recognizes this material as a medium of exchange of knowledge, news, and correspondence, and as a means of recording historical facts, business transactions, etc. Without it or a good

substitute for these purposes, our present civilization could hardly exist.

It is not so well known that in recent years paper has found a wide use in other than printing and writing fields, as a substitute for a variety of materials. It is not a case of the substitute being better than the original in all instances, but the substitution has been carried far enough to cause considerable inconvenience if paper could no longer be had. Paper-insulating material, twine, furniture, rugs, towels, and food containers are examples of recent innovations. One of the most startling during the World War was the use of paper clothing. Perhaps the most welcome substitution to the women, and some men, would be for dishes, and they will hail the day when the set of paper dishes, knives, forks, and spoons can be made so cheaply that they can be discarded after every meal.

Many important cellulose products, such as guncotton, artificial silk, imitation rubber, and collodion, which heretofore have been made from cotton fiber, are now being produced from wood fiber. Since the production of cellulose fiber from wood comprises a large part of the paper industry, the manufacture of these products from paper-making material further emphasizes the important part the products of the pulp and paper industry play in our daily life.

In spite of the fact that chemistry has been applied to the paper industry quite vigorously, especially in the past quarter of a century, there are still several unsolved problems which command the attention of the chemist.

Opportunities for Chemistry

Probably the greatest of all is the waste liquor problem in sulfite mills. The nonfibrous portion,

which is dissolved in the cooking process, represents approximately 50 per cent of the weight of the wood. Consequently, 50 per cent of the raw material of the sulfite proces is wasted. In 1922 there were 5,550,000 cords of wood used in this country. Of this amount two million cords were used for newspaper, leaving three and one-half million for chemical pulp. Since a cord of dry wood weighs about 2200 pounds, the loss in one year was nearly four billion pounds.

Here is an example of waste similar to that which existed at one time in the coke industry when millions of dollars worth of valuable by-products were lost from beehive coke ovens. The paper industry is eagerly waiting for some method of utilization of sulfite liquor which will enable it to turn this waste into a valuable by-product. Much work has already been done along this line and while several interesting developments have resulted, the real solution has not yet been found. It might be of interest to mention that grain alcohol, dyestuffs, medicinals, and explosives can all be secured indirectly but at considerable cost or in small quantities. The liquor in dilute and concentrated form can be used in various ways, such as a binder, fuel, and fire extinguisher compounds.

Bark from the trees represents another problem. There is no useful fiber in it, and therefore it must be removed from the woody portion before pulp making begins. This means that 15 per cent of the weight of the material of the tree must be eliminated. No matter whether taken off in the forest or at the mill, it is waste material. No good use has as yet been found for it—no means of converting it into a useful product. It can be, and is, burned, but not with an appreciable saving in fuel, since it carries so much water

from the barking process that it sometimes requires other fuel to burn it.

More knowledge of the chemistry of the cooking process is highly desirable in order to secure a higher yield of fiber, to be able better to control the process, and to eliminate undesirable constituents of wood, such as resins which are present in small quantities.

The importance of the sizing process in giving the quality of ink resistance to the paper is fully recognized in the paper industry. While good results are being obtained with the existing knowledge of the chemistry of the process, it is very desirable to have a better understanding of it. This can come only through further study.

Chemistry may be called upon again to supply new raw material. When wood was first introduced, it was thought that we had an inexhaustible supply of wood for pulp, but the heavy demand for it, both as a structural and as a paper-making material, with a lack of a reforestation policy and the enormous losses through fire and pests, have brought the end of the forests, in some locations, within calculable limits. However, the rapid depletion of the forests has been something of which the paper industry has been well aware for some years. Even though the consumption of wood for paper making is a small amount of the total, strenuous efforts have been made by this industry to preserve the supply and to encourage reforestation for future needs. Nevertheless, the policy of conservation carries with it the obligation to secure greater production through present and new cooking methods, to reduce conversion losses, and to use, in larger quantities, materials such as straw and grass.

These unsolved problems are all the more interesting because so many different phases of chemistry are

involved; also because problems of a highly theoretical nature and those requiring application await attention. The molecular weight of cellulose is still unknown. The principles of colloid chemistry have not yet been applied. Thus there are many ways in which chemistry can still contribute to an industry which has already derived many benefits from it.

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CHAPTER XVI

PERFUMES AND FLAVORS

S. Isermann

President of Van Dyk & Company and The Chemical Company of America

The use of perfumery and toilet preparations plays an important rôle in our daily happiness, as the smell of pleasant and attractive odors makes us forget part of life's struggles and helps to keep us young and beautiful. A person who dislikes agreeable scents of every sort must be an inartistic and grouchy individual who does not appreciate the harmonious things in life.

Chemistry, more than anything else, should be given credit for the state of perfection attained in perfumery and flavors within the past quarter of a century, thereby adding to the convenience and happiness of humanity. A great many experiments, covering a number of years, have been made on the mental reaction to odors. These experiments were conducted by celebrated physicians, great writers like Zola, Tolstoy, etc., and such investigators as Zwaardemaker, Henning, and others—each one tackling the problem from a different viewpoint, but reaching practically the same conclusions.

Recently, J. H. Kenneth of England has undertaken the study of the psychological and physical effects of odors, and under the title "Some Experiments on

Mental Reactions to Odors" reviews a number of experiments carried out through the Carnegie Research Fellowship in the Psychology Department by J. Drever, of Edinburgh University. More than sixty men and women students acted as subjects.

To begin with, it was found that odor preferences, while subject to fluctuations, could be determined with some degree of accuracy.

The factors determining the pleasantness or unpleasantness of an odor are partly inherent in the osmyl (odorous substance) itself, e.g., molecular wave length (as determined by absorption bands in the spectrum), quantity of molecules, etc.

Other determining factors are, racial instincts, state of physical and mental health and other anatomical and physiological qualities of the person receiving the stimulus.

Sounds may produce an effect similar to that produced by a perfume, and so there are cases where perfumes conjure up melodies.

The olfactory sense has been very much neglected as far as conscious mental life is concerned.

In the nose we have an extremely delicate smelling-in set, which, if properly tuned up, is capable of receiving messages from innumerable broadcasting stations.

This article by Kenneth also reaffirms the statements made by previous investigators who have found that different races prefer different perfumes (the same is true of spices entering into food). It can be authoritatively stated that people of the same physical and mental make-up have a preference for certain odors. It has been found further that women can differentiate the quality of odor better than men, but the reverse is true with respect to quantity of odor. This is a strange phenomenon, since men, because of their occu-

pations and daily habits, should become less sensitive to odors.

Although perfumes are used chiefly for their agreeable odors and the pleasant sensations they create, the hygienic side of perfumery must not be overlooked. Every volatile oil used in perfumery possesses antiseptic qualities. As will be shown later, many oils used for perfumery and flavors are from ten to twenty times as strong in their antiseptic qualities as phenol, commonly called carbolic acid.

History

Perfumery is of great historical interest and dates back to almost 3000 B. C. There is hardly an occupation or an industry which has prevailed through the centuries as has the perfumery industry. Odorous materials, such as aromatic gums and spices, have played an important role in the life and trade of the peoples of the earth. In the days of antiquity, world trade was carried on in aromatic substances, and, strange as it might seem, some of these substances even today are recognized products used in the manufacture of scented articles and in the aromatizing of foods. The same spices—cloves, allspice, cardamom, cinnamon, etc.—which have been used for centuries and centuries, are still being employed in the preparation of savory sauces for our daily food.

Documents have been found which prove that about four thousand years ago, 2100 B. C., in the days of Hamurabi, perfumery was ordered as a compulsory measure by the Babylonians to be used by their nurses and even distributed to their servants in the form of scented or perfumed salves or ointments. The Babylonians, Egyptians, and Jews annointed themselves

with scented ointments and burned aromatic gums and spices in their temples. The burning of incense (olibanum) in the performance of certain religious rites is probably the only ceremony of its kind remaining from the days of old.

Spices and other odorous substances were also used for fumigating purposes. It is said that King Solomon placed in his temple forty thousand fumigating receptacles, hammered out of silver and gold, for use in the performance of certain ceremonies.

In those days when kings and queens from various lands paid tribute to one another, friendship and admiration were shown in the way of bringing gifts, consisting mostly of jewelry, precious stones, and pearls. But aromatic gums, spices, scents, and fine aromatic substances, or perfumes, as we might call them today, were considered the finest gifts that could be offered.

There is no wonder, then, that a world trade was carried on in these commodities and that, historically speaking, the perfumery and flavoring industry as such stands second to none in the world. Anyone who is interested in the history of perfumery and aromatic gums and spices, and their effect on our civilization, can procure a number of books on the subject in the public libraries.

Steam distillation used today in the arts and sciences was invented and first used in the production of volatile or essential oils. This art was not known in Europe until the early part of the sixteenth century, when essential oils were produced by distillation of certain herbs, roots, petals, aromatic seeds, etc. Even today, the civilized nations gather materials containing aromatic principles from all parts of the world. This is especially true of the tropics where the growth is abundant and labor is reasonable, but

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Das büch der waren kunst zü distillieren die

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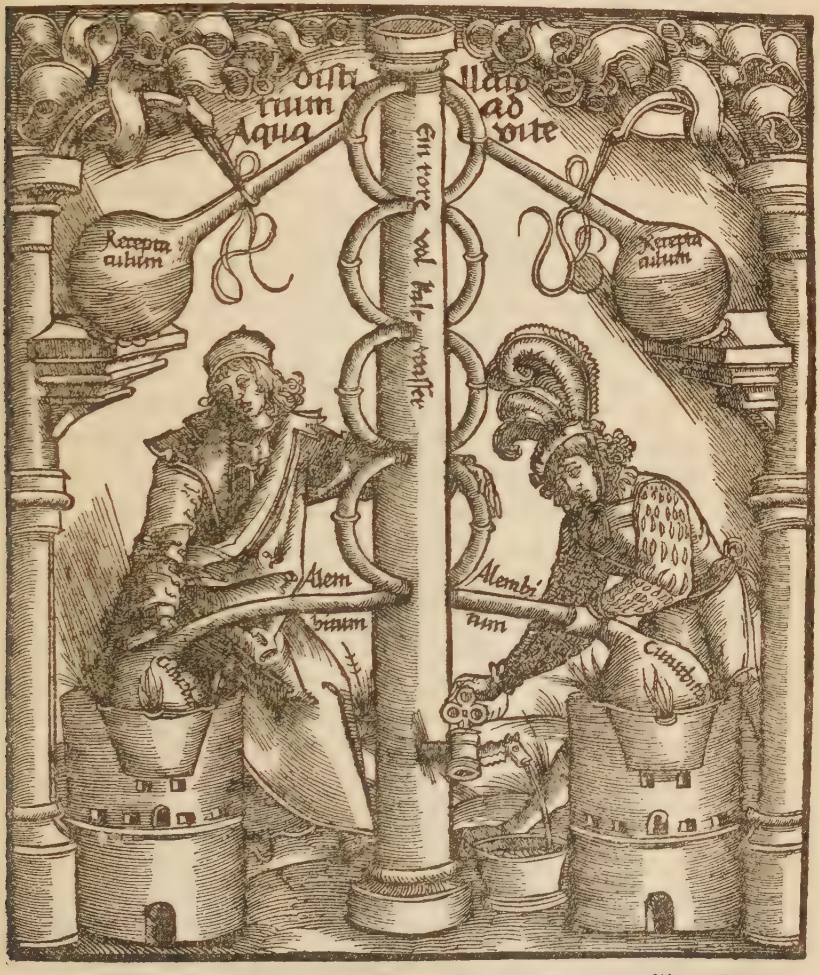


getruckt un gendigt in die keisserliche frye statt Strassburg
uff sanct Mathis abent in dem jar 1507.

Ancient Cover Page of a Book on Steam Distillation Published in 1507

Reprinted by permission from "The Volatile Oils," by Gildemeister and Hoffman.
Published by John Wiley and Sons, Inc.

as George Cohn, in his book "Die Riechstoffe," says, "The history of perfumery is ancient, but the older its history, the younger the history of its chemistry."

In Europe the art of perfumery was lost for several centuries and was again introduced when travelers from the Byzantines brought over gifts of aromatic essences and oils for their wives and sweethearts.

Definition of Terms

Before discussing the effect of chemistry on the perfumery and flavoring industry, it is necessary to explain what we mean by perfumery. By this term today is meant making mixtures or blending aromatic substances in such a way as to make them agreeable and pleasant to the olfactory nerves. These blends are dissolved or mixed with carriers such as ethyl alcohol, or cologne spirits, as it is called by perfumers, and powders such as talcum, rice, starch, chalk, and other similar substances.

In general, the raw materials used in the manufacture of these perfumes or perfumed articles are called aromatic or odorous substances. While all products used for the creation of scented articles are of a chemical nature, they may be divided into three classes: (1) natural products of vegetable nature; (2) natural products of animal nature; (3) perfumery chemicals.

Natural Products of Vegetable Nature

Flower products are extracted from flowers by means of solvents, France being the principal country of production. The solvents used are purified gasoline, benzine, alcohol, etc.

The climate of southern France, in the region of

Grasse and Cannes, is best adapted to the growing of these flowers, and the manufacture of flower products is of considerable importance to the industries of France. France, owing to its favorable climate, has followed this industry for a great many years. The gathering of the flowers is carried on mostly by women and children. Labor, which plays an important role in the gathering and production of these flower products, is at a minimum in southern France.

In the old days, before chemistry entered the field of perfumery, the flowers were gathered and spread on purified lard. The lard was later heated and strained and the process of odor absorption and extraction from the lard was repeated several times; the finished product was called pomade. This pomade found its way into the market and was used by perfumers the world over. The chemists entering into the field discarded this method of operation and introduced methods of extraction with volatile solvents, the operation being simpler, more effective, and resulting in better products. The pomades have been almost entirely discarded by the perfumers of the world.

When the lard was afterwards extracted with cologne spirits of alcohol, in order to get out the perfume, a certain amount of lard went into solution with the perfume and had to be later frozen out. This freezing-out method, however, was never complete and, therefore, in the old days perfumery would become rancid in a short time. This rancidity of perfumes is entirely avoided by the adoption of modern methods of extraction. The producer of flower products, while at first mistrusting the chemist who, he thought, was going to interfere with his livelihood, eventually found him a great aid to the industry. Today in a certain section of France great prosperity exists, mainly due

to the sale of perfumery flower products which are manufactured by the most modern methods.

Through the activities of the organic chemists who have specialized in perfumery materials, the refinement of the flower products has been made possible, with the result that the perfume industry has grown to tremendous proportions. The growers and manufacturers of flower products are availing themselves of the privilege of being able to buy chemical substances suitable for their purpose and are today blending certain of their flower products with synthetic chemicals in order to make them more uniform and more attractive to the consumer.

It is an interesting fact that the producers of flower products in France have become important consumers of perfumery chemicals. Twenty or twenty-five years ago the manufacturers of flower products and their representatives discouraged the use of perfumery chemicals. Today they are offering these materials freely. The reason is that these manufacturers, whether large or small, have found that they need the chemicals to improve their natural products, and furthermore, that they cannot exist without the manufacture and sale of the chemical perfumes.

Essential or volatile oils, also known as perfumery oils, are produced by distilling with live steam certain herbs, leaves, seeds, buds, roots, flowers, etc. However, a few oils like orange, lemon, and bergamot are not produced by steam distillation, which breaks down and interferes with the aroma or flavor of the oil. These are therefore obtained in the cold, as all of the flavor or oil is present in the peel of the lemon, orange, or bergamot, and not in the pulp and juice, which are composed principally of citric acid. The oil is obtained by the simple process of breaking the

oil cells by scraping the fruit with a sharp instrument. In this way the oil is freed from the peel and then thrown into cold water; as the oil floats on the top it is separated by ordinary mechanical methods.

This method is still being employed in Italy where practically all of these oils are obtained. In 1913 and 1914, the manufacture of lemon and orange oils was started in California; this undertaking has met with considerable success. Orange oil is also made in the West Indies, but is not considered so good as Italian oil. However, it has successfully found its way into the markets.

STEAM DISTILLATION

The process of steam distillation is a simple one. It is carried out by placing the product to be distilled usually in a copper still, filling the still with water and heating to the boiling point, condensing the vapors, col-

Antiquated Bulgarian Distilling Apparatus Used in Distilling Rose Oil in Bulgaria Today

lecting the oil mechanically, and separating it from the distillate with ordinary separators. In this way the volatile or essential oil is freed from the flower, leaf, root, herb, seed, etc., and by simple mechanical means is carried over with the water. The essential oil, being usually lighter than water, floats on top and is after-

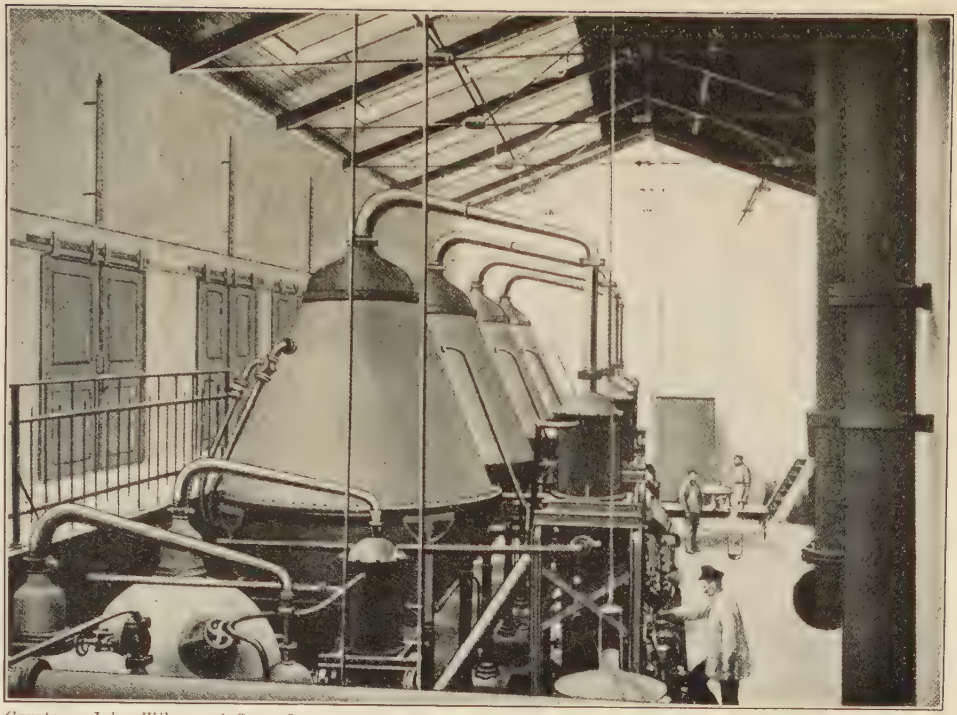
wards separated by means of mechanical separators or separatory funnels.

Steam distillation has been carried out for hundreds of years, and while refinements have been made in the process the principle remains the same. It can be readily seen that complex chemical substances which make up these essential oils are very often broken up and destroyed during the process of steam distillation.

As these oils are gathered from various parts of the globe and distillations are carried out in the interior of tropical countries, often in movable stills, the methods used even today are antiquated and it will be a great many more years before material changes or improvements will be effected. With no facilities on hand and with cheap and plentiful labor, progress is naturally slow. Furthermore, most of the products distilled in those countries are low priced on account of the inferiority of the odor, so that in a great many cases extraordinary care is not of utmost importance.

In some cases, however, even the distillation of expensive oils is still carried out in an antiquated manner. This is especially true in the case of the well-known and much discussed oil of rose (attar of roses). This oil for a great many years was recognized as the principal perfume oil of the world. Attar of roses has been known since the earliest periods and the charm and fragrance of the rose flower has led to its appreciation and use. In the olden days before the chemist entered the perfumery field, the rose perfume received preference over all odors. In Chinese and Sanskrit literature, the fragrance of the rose is often described.

The methods used in Bulgaria and Turkey for the distillation of oil of rose were most antiquated until fifteen or twenty years ago, and even today there are



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Modern Rose Oil Still.

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certain sections in Bulgaria and Turkey where methods of distillation are still carried out as of old. Bulgarian rose oil, as it is ordinarily called whether obtained from Bulgaria or Turkey, has a great reputation and is used in the manufacture of perfumes, in the flavoring of tobacco, especially snuff tobacco, and in a minor degree for other flavoring purposes as in candies, etc. The price of rose oil depends upon crop conditions and the demand. It fluctuates from three dollars up to ten dollars per ounce. At certain times the price has even gone up as high as fifteen and twenty dollars per ounce.

One of the principal ingredients of attar of roses is a chemical product now made out of toluene, a coal-tar distillate, and is called phenylethyl alcohol. This phenylethyl alcohol is the principal odor contained in rose water and is the distinctive constituent of dried rose leaves from which they get their peculiar rose odor. Should anyone carefully compare the odor of the oil as obtained from Bulgaria with the odor of the rose flowers grown in our gardens, he would immediately find that there is something lacking in the rose oil. The reason is that phenylethyl alcohol, the carrier of the rose odor, is soluble in water, and during the ordinary process of steam distillation, as carried out in Bulgaria, most of this phenylethyl alcohol stays dissolved in the water and is afterwards sold as rose water.

Modern distillation plants established in those countries in the past few years separate this water from the oil in small containers and return it automatically to the still without handling. In this way the loss of phenylethyl alcohol in the oil of rose is minimized. In France and Germany where similar rose oil is produced, the most modern stills are used and all of the

phenylethyl alcohol and other vital products contained in the water are returned to the still.

The literature on oil of rose is voluminous, entering into the questions of purity of product, its falsification, chemical methods of detecting adulteration, etc. The natives who gather the flowers and distil the oil have found means of falsification so that a pure oil from natural sources is very difficult to obtain. For this reason, careful purchasers of rose oil buy known brands only. It is interesting to know that, depending upon crop conditions, it takes from 250,000 to 750,000 roses to produce one pound of Bulgarian oil of rose. Since, contrary to former beliefs, most of the essential oils are not composed of single constituents, but contain a great number of bodies, which have been chemically isolated, it can be readily seen that the production of the high-priced essential or volatile oils, such as rose, ylang-ylang, and others which are carried out by nonscientific people, is subject to poor handling and a great many falsifications, making these products most unreliable.

Natural Products of Animal Nature

AMBERGRIS

In the manufacture of perfumery a few animal products are used, the most important of which is probably ambergris. This substance, while seemingly not very strong in odor, is used on account of its binding or blending qualities.

Ambergris is a fatty secretion formed in the bowels of certain sperm whales; sometimes taken from whales directly, but more often found floating in the Thracian waters, or in other waters of the tropics frequented by these whales. It is often cast on the beaches

in lumps of different sizes. (Masses have been found to weigh as much as 200 pounds.) When taken from the whale it has a very disagreeable and fatty smell, but upon oxidation by the air it develops a sweet earthy odor.

Although the chemistry of ambergris is fairly well known, it has never been synthesized. Ambergris at one time was considered quite an important drug. A good quality is valued up to four hundred dollars a pound and for this reason is very often adulterated. Occasionally large lumps of ambergris of different qualities are brought to eastern ports, especially around Boston.

In accordance with the old custom, the skipper and the crew of a whaler finding an amount of ambergris are entitled to the find. The skipper divides the proceeds with his crew. Naturally, on account of the value of the ambergris, it can be readily seen that most whalers become treasure hunters and have a dream of sometime in their life finding a large amount of ambergris. There are but few persons in the world who are considered experts on the quality of ambergris and for that reason there are few wholesale purchasers. It is therefore left to a small number to buy this material, and as one lump is often composed of several qualities, the purchaser finds it necessary to separate his purchase in several grades, and in that way realizes considerable profit. It is also for this reason that the purchase of large lumps of ambergris is considered a gamble.

MUSK

An interesting product is musk, which is obtained from the musk deer living in the high Himalayas, Tibet, and eastern Siberia. This animal stands about

twenty inches high and has a very clumsy form. The musk deer's favorite haunts are on the tops of pine-covered mountains and in some places extend far above the region of the pines. He is extremely timid and is pursued by hunters largely on account of an odoriferous secretion called musk, which has been known in Europe since the eighth century.

The exterior of the deer's musk pod or bag is composed of a number of glands containing musk in the form of grains. The grain musk is very often deposited by the musk deer on stones and is picked up by the natives and prepared for the market. Purchasers, however, prefer to buy the whole pod or bag. In days of old, a tincture made of the grain or pod musk was considered a potent drug and used in the treatment of nervous diseases, fever, and epilepsy. In later years, the use of musk as a drug has been practically discarded.

It is, however, considered a very important substance in the manufacture of perfumery, where it is used as a binder and blender of odors. Pure musk sells at two hundred and fifty to three hundred dollars a pound and, because of its price, is subject to adulteration by the native Chinese who collect the product for the market. The adulteration or falsification is carried on in various ways. The pods, for instance, are subject to an injection of tin or lead, in that way increasing the weight.

CIVET

Civet is a fatty substance derived from the civet cat, a carnivorous animal, sometimes spoken of as a cross between a cat and a hyena. The best species of this animal giving the finest grade of civet is a native of northern Africa. It is about two or three feet long

and is of brownish-gray color with numerous black stripes or spots. The animal feeds on birds, reptiles, crocodile eggs, etc., and for that reason is regarded as a benefactor of the Nile.

Many of these animals are kept in captivity for the purpose of collecting the fatty substance for use in the production of perfumery. While the amount of civet contained in the bag of this animal is small, under certain conditions by annoying these animals greater amounts are obtained. Natives collect and pack it in horns of steers containing from twenty to eighty ounces each.

Civet has a very disagreeable odor, but nevertheless is a recognized fixative or blender for perfumes. Its price ranges from twenty to forty dollars a pound. Because of its price and the impossibility of procuring it elsewhere, the natives of northern Africa take advantage of this situation and adulterate or falsify the civet to a very great extent. Therefore, civet brought into the markets of the world is purchased by dealers who are recognized experts in the field.

Civet, as well as the two previously mentioned animal products, has been investigated by chemists for a great many years. While the substances which produce the principal odor are known, up to the present moment, in the mind of the perfumer or chemist, no real substitute for civet has been found.

CASTOR

In previous years, castoreum, or castor as it is sometimes called, was used in perfumery. This substance is obtained from a certain type of Russian beaver, an animal which is becoming extinct. Castor was used in the days of Hippocrates as a medicine in treating

nervous diseases, hysteria, epilepsy, etc., but since the invention and manufacture of the new coal-tar remedies, castor, together with other useless drugs, has been thrown into the discard. The perfumer has also found that there is very little virtue in castor.

Perfumery Chemicals

The substances which the perfumer calls synthetics or synthetic aromatic chemicals are manufactured products of a definite chemical nature—each substance being definite in its specific gravity, boiling point or melting point, optical rotation, etc.—and therefore should not be confused with the so-called artificial substances, which are usually mixtures.

Up to the time the chemist took up the study of perfumery materials, about forty years ago, it was considered that essential or volatile oils, flower products, and other similar substances used by the perfumer were individual or single substances or chemical bodies. In other words, each extraction or distillate produced and used in the manufacture of scents and flavors was supposed to be a single product and not a mixture or combination of chemical products created in Nature's laboratory.

As an illustration, let us take the oils expressed out of lemon or orange peels, used for flavoring beverages, ices, and puddings, and in the manufacture of eau de cologne. In 1884, when Theodore Wallach undertook the investigation of the essential oils and isolated or separated these oils into their different chemical constituents, such oils as lemon, orange, etc., to his great surprise, were found to be composed of a great number of substances, each one of a different chemical nature. Some of these substances are responsible for the lead-

ing note of the odor; others act as carriers; and some are resinification or break-down products, which, instead of helping, were later found to interfere with the quality of the odor or flavor. The principal odor of lemon, for instance, is due to an aldehyde called citral. Lemon oil contains from 6 to 7 per cent citral and over 90 per cent of a diluent, lemonine, a useless turpentiny substance or terpene. The rest is made up of small proportions of aromatic alcohols, ethers, and aldehydes. Orange oil is composed of 95 per cent of lemonine, the balance being made up of citral and other aldehydes, alcohols, traces of fine smelling esters, etc.

Take the well-known peppermint oil which is mostly used as a drug and for flavoring purposes. Its principal constituent is menthol or esters or ethers of menthol. The manufacture of peppermint oil is carried on in the States of Michigan and New York on an extensive scale, and all good qualities of this oil are exported to a great many foreign countries. The fine flavor of the peppermint oil is due to the menthol and the weedy taste to the terpenes. The total number of distinct chemical substances contained in American peppermint oil is about thirty.

Thousands of essential oils have been investigated by a great many organic chemists; the component parts of these oils have been isolated and duplicated by chemical means. Some oils have been found to be composed of twenty-five or more distinct chemicals produced in the building up or breaking down of the aromatic substances by Nature. These substances find use either as spices, perfumes, drugs, or flavors.

While Wallach and other purely theoretical investigators of his type were carrying on these very important scientific investigations, another set of chem-

ists at the same time started to investigate along practical lines—namely, the method of building up new chemical products suitable for perfumery or flavors. Of these investigators Tiemann, von Bayer, Barbier, and Bouveault deserve most credit.

This work not only resulted in practical production of most valuable chemical products, but also proved a successful financial undertaking to a number of manufacturers. Wallach and Tiemann, however, are really the ones who started investigations on this class of organic chemicals which were later continued by Semler, Hesse, and others and through their untiring effort and tedious work opened up a way for new chemical research. This research and investigation must be considered epoch-making, since a great number of chemical substances used in our daily life and occupation are the results of their findings. These discoveries not only are useful in this line of work, but are of great value in the development of the synthetic drug, dye, photochemical, and rubber-accelerator fields, etc.

In the perfumery field, the chemist, first having analyzed the constituent parts of the aromatic essential oils and flower products, started out to reproduce them chemically, carrying on research and experiments along specific lines. In view of the different methods of manufacture of chemical perfumery materials, they should be divided into three classes, as follows: (1) substances isolated from natural products; (2) cheap natural products converted into valuable perfumery chemicals; and (3) coal-tar products.

SUBSTANCES ISOLATED FROM NATURAL PRODUCTS

In the first class, the chemist makes use of different chemical reactions and isolates the valuable substances

from the worthless ones contained in the natural essential oils. In order to do that he uses different chemical and physical methods, such as fractionation, distillation, crystallization, and chemical combinations.

To illustrate, citronella oil, which has a very disagreeable odor and is often used for the driving away of mosquitoes, contains among other things a substance called geraniol. Geraniol itself is a very pleasant, rose-like smelling body contained in natural rose oil up to 50 per cent. Citronella is a very cheap oil selling from fifty cents to one dollar a pound. It will be remembered that attar of roses sells for as much as two hundred dollars a pound. Geraniol is isolated from the citronella oil by chemical treatment, distillation, and crystallization. The crystal, which we will say is the calcium salt, is washed with ether or alcohol, decomposed or broken up, and the geraniol is steam-distilled and purified by distillation in a vacuum. Geraniol has become a very valuable product of perfumery and is used in the blending of rose odors for making so-called synthetic rose oils, etc.

The fine flavor of cassia or cinnamon oil is due to a well-known product called cinnamic aldehyde. Cassia oil as such is used mostly for perfuming cheap soap and not for flavoring purposes. As cassia oil is brought into the market in lead receptacles, it contains traces of lead and cannot be used for flavoring purposes, both because it lacks the fine flavor of cinnamon, and because the traces of lead render it poisonous and unsuitable for food purposes.

Before cinnamic aldehyde was produced chemically from coal tar, in order to make a fine cinnamon flavor the cinnamic aldehyde contained in cassia oil had to be shaken out with bisulfite of soda. This method produced a solid cinnamic aldehyde compound, which

was washed free from impurities and afterwards broken up and purified by steam and vacuum distillation.

In a similar way, menthol, an important drug and anti-neuralgic, is extracted or frozen out of cheap Japanese peppermint oil, an oil which is practically useless for any other purpose. American peppermint oil is a much finer flavored product, but contains less menthol. Japanese peppermint oil, on the other hand, has a very poor flavor, but since it is very rich in menthol content the Japanese are converting most of it into menthol. The Japanese Government considers menthol production one of its important industries, and therefore the manufacture of menthol, as well as camphor, is controlled by the Japanese Government. Of late a process has been invented to manufacture menthol chemically or "synthetically," as it is termed.

Camphor is a substance used in the manufacture of celluloid, and until very recently the Japanese Government, on account of its camphor monopoly, controlled the celluloid industry completely. A chemical process was devised a few years ago which makes it possible to produce camphor synthetically from turpentine. It is believed that because of this competition the Japanese Government is losing money on its camphor production.

CONVERSION OF CHEAP TO VALUABLE PRODUCTS

In the second class the chemist has found ways to combine a number of cheap products which he has isolated from natural sources, thus creating new chemical bodies. This method has become of great value. To that category belong some of the greatest inventions in the perfumery field.

Take, for instance, the very interesting product

called ionone, invented by Tiemann. In olden days, when violet perfumes were manufactured from orris root, Tiemann started out to investigate the production of irone, the active or odorous ingredient of orris root. He succeeded in producing the same chemical body—that is, a body containing the same number of carbon, hydrogen, and oxygen molecules—but instead of building them up synthetically, he added citral, a substance previously mentioned as contained in lemon and orange oils, which, however, he isolated from the very cheap lemon grass oil grown in India. Lemon grass oil contains up to 75 per cent citral, and on account of its unpleasant and disagreeable odor very often sells at about fifty cents a pound; at present it is worth about one dollar.

As stated, Tiemann combined lemon grass citral with acetone and produced a new chemical compound containing the same number of carbon, hydrogen, and oxygen molecules as irone, but to his great surprise he found that the substance so produced was practically odorless. Having in his hands both substances presumably of the same chemical nature, one having a wonderful odor of orris and the other odorless, he proceeded to experiment with the new substance. By treating it with acid he managed to change the position of the molecules, and to his pleasant surprise he got a product that, while remotely resembling the odor of orris, in dilution had a distinct violet odor.

This product he named "ionone." The invention of the manufacture of ionone was sold by Tiemann to a large French and German concern who proceeded to market it; and it was due to this great invention that the perfumers became vitally interested in chemical perfumery materials. But, as is true of all great inventions, it took the old-time perfumers a long time

to see the value of this new product. A large French firm saw the light and contracted with the Tiemann firm to supply it with ionone exclusively for a number of years. That was a chance to introduce a new violet perfume in the market. The perfume and the company became famous and held the market for a great number of years.

After the expiration of the contract with this French firm, ionone was brought into the market by the Tiemann firm and sold in the United States at one hundred and twenty-eight dollars a pound for the 10 per cent solution, or twelve hundred and eighty dollars a pound for the 100 per cent product. As a matter of interest it might be said that a better product than the old 100 per cent ionone, which sold at twelve hundred and eighty dollars a pound, sells today at less than ten dollars a pound.

On a similar basis this method of development continued, and a great number of products were built up by isolating cheap chemical bodies from natural sources and combining them with strictly chemical products, resulting in the creation of a whole series of new important perfume bases. It is this class of work that is also responsible for the building up of synthetic or chemical flower products—e.g., lilac, lily of the valley, and a whole series of new bouquet odors. So far as the true odor of violet is concerned, new acetylene products invented by Moreau smell much better than the flower itself, and it takes but a few drops to get the desired results.

COAL-TAR PRODUCTS

The third and last class consists of coal-tar products. It is expected that this field, being the most fertile one for the perfume chemist, will bring forth the greatest

successes of the future. To this class belong such important flavors and perfume materials as benzaldehyde or artificial bitter almond oil, and benzyl acetate, a substance smelling like jasmine made from toluene and chlorine.

Benzyl benzoate and benzyl alcohol, also made from toluene, were first brought into prominence by perfume chemists as solvents useful in perfumery. Both of these chemicals are contained in a great number of flower products and natural perfumery substances. During the war the usefulness of benzyl benzoate and benzyl alcohol became known in this country and abroad as high-boiling solvents for the softening of airplane wings in order to make them weatherproof. But this is not all!

About 1918, an American scientist named Macht, of Johns Hopkins University, discovered their use in medicine. He found that benzyl benzoate and benzyl alcohol have the same pain-allaying properties as some of the constituents found in opium, but have none of its narcotic qualities and are not habit-forming. Benzyl benzoate is recommended for asthma, whooping cough, etc. Benzyl alcohol, on the other hand, is used as a local anesthetic for allaying pain and in the performance of minor operations. It is also the newest toothache remedy. Balsam tolu, derived from the South American tolu tree, has been used a great many years for coughs and colds. The well-known children's cough medicine (Stokes Cough Mixture) contains this balsam. The constitutents to which it owes its medicinal action are benzyl benzoate and benzyl alcohol.

Phenylethyl alcohol, a chemical substance previously mentioned, is contained in natural attar of roses, rose water, etc., and is also made from toluene, chlorine, and cyanide of potash or soda. Rose water,

which contains phenylethyl alcohol, is often used as a sleeping potion for children. Its effect, no doubt, is due to the phenylethyl alcohol. In later years phenylethyl alcohol has been tried as a local anesthetic in minor eye operations.

Coumarin, contained in the tonka bean and chemically produced from phenol (carbolic acid) or cresol, is used for the flavoring of tobacco, in the manufacture of perfumes and cheap household vanilla extract. It is also a principal ingredient in a drink called "May-wine," a beverage probably out of existence in the United States.

Another important flavoring material, also first produced by Tiemann, is vanillin. This valuable flavor and perfume is used in the manufacture of various ices, cakes, and biscuits, as well as for perfumery purposes. Vanillin when first introduced sold at fifteen dollars an ounce or two hundred and forty dollars a pound. The market price today is about fifty cents an ounce, or about eight dollars a pound. There are two reasons for this: First, the chemist has learned how to manufacture a better and cheaper vanillin; and second, several products when first put on the market were patented and the foreign owners of the patents in exploiting their inventions desired to make large profits.

While vanillin as manufactured today in the majority of the plants in various parts of the world—e.g., Germany, Switzerland, France, England, and the United States—is made mostly of eugenol, a substance of a phenolic nature contained in clove oil, the latest method of production is from benzene, a coal-tar product, and it is for this reason it is mentioned at this time. In chemistry it makes no difference what the

starting point is so long as the final product is the same.

If a chemist can combine toluene, a coal-tar distillate, which smells like gasoline, with chlorine, one of the poison gases used in the war, and by treating it with another deadly poison, cyanide, make a wonderful smelling and nonpoisonous health-aiding substance called phenylethyl alcohol, or can treat benzene similarly and produce the fine flavor of vanilla beans, vanillin, one can rightfully ask—when and where is chemistry going to stop and what has the future in store for us?

But the most interesting of all is artificial musk. This is a very important perfume chemical and has absolutely no relationship to the natural musk, chemically or otherwise.

In 1888, Bauer invented a process for the manufacture of a product he called musk. This product must be considered related to the high explosives. One of the best known explosives used during the war was picric acid. Chemically it is trinitrophenol, or carbolic acid containing three nitro groups. The most important of all explosives during the World War was a product called TNT or trinitrotoluene, toluene containing three nitro groups. The synthetic musk as invented by Bauer is trinitrobutyltoluene or trinitrobutylxylene. The difference between artificial musk and the high explosives is that, aside from the three nitro groups, it also contains butyl alcohol, a by-product obtained in the distillation of grain or ethyl alcohol.

The artificial musks, on account of their explosive nature and the use of concentrated nitric acid in their manufacture, are produced on a small scale. Plants manufacturing artificial musk often have fires or ex-

plosions. Therefore, the manufacture of musk is isolated in very small buildings so that in case of fire or explosion the loss will not be serious.

When musk was first introduced, it sold around ten dollars an ounce or one hundred and sixty dollars a pound, and the product contained no more than 10 per cent musk. In other words, the musk on the market was composed of ten parts of musk and ninety parts of acetanilide, a drug and nonodorous material. At that rate, the 100 per cent product figured about twenty-five hundred dollars per pound. In those days, perfumers buying musk or ionone would immediately lodge it in a safe deposit vault, as they were afraid that someone might steal it. Today a better musk than the original product sells as low as four dollars a pound for the 100 per cent chemical.

Because of the outrageous prices charged by the firms who exploited these patents, countries such as Switzerland and Holland, which had no governing patent laws, became hotbeds of commercial piracy. Firms started up all over Switzerland and a few in Holland to manufacture musks, ionones, vanillin, saccharin, etc., and through subterranean channels managed to smuggle them into various parts of the world—wherever they saw a demand for these products—underselling the original makers by one-third or one-half, and still realizing a good profit.

Today the original Bauer musk is not considered of great value, since finer grade musks have been put on the market, one called keton musk and another ambretté musk. This latter more powerful substance is produced from cresol, instead of xylene or toluene, and has the odor of both musk and amber.

But these better products, even though worth a great deal more than the old musks, do not bring fancy prices

today, the highest price possible being about fifteen to eighteen dollars a pound. Ambretté musk in a way is also an explosive, being a trinitro body—namely, trinitrobutylcresol. Today the artificial musks are recognized as the principal fixatives or blenders of perfumery. While a few years ago the perfumer discouraged the coöperation of the chemist, if a perfumer were told today that it was necessary to get along without artificial musks, no doubt he would say that his business would be ruined, because his perfumes would lose their commercial value for lack of lasting qualities.

One might go on indefinitely relating great discoveries made by chemists in this field. Take saccharin, for instance, a sweetener and flavor first discovered by Dr. Ira Remsen of John Hopkins University, afterwards transferred to Germany through one named Fahlberg, and by many considered as a German invention. Saccharin, produced from the coal-tar distillate, toluene, is from five hundred to five hundred and fifty times as sweet as sugar. If it were not for saccharin, diabetic persons, who are prohibited from using sugar, would be compelled to take their tea, coffee, and other foods without a sweetener.

As a sweetener, it is of just as much value as sugar. Some years ago there was considerable controversy on the use of saccharin for food purposes. Its use was prohibited, not because of its deleterious nature, but, being just a sweetener, it could not be considered a substitute for sugar, which is a food supplying heat to the body. During the war, when the sugar was limited and it was impossible to carry sufficient amounts to the front, saccharin became a part of the rations of the soldier.

Relationship between the Perfumer and the Perfumery Chemist

From the foregoing, the functions of the perfumery chemist and his relationship to the perfumer can be clearly seen, but it has not been made clear whether a chemist manufacturing perfumery materials must be a perfumer, or whether a perfumer who manufactures the finished product need be a perfumery chemist.

If organic chemists manufacturing perfumery materials master the art of blending, they are most invaluable to their profession. The reason is that when a chemist brings out a new perfumery chemical, in order properly to introduce it on the market he must be able to demonstrate its use. This requires an investigation to be undertaken by a person who knows perfumery and has the experience and a trained nose.

To find the proper way to use a new chemical perfume product becomes the perfumer's task. In other words, the chemist is the scientist who invents or creates new chemical products of perfumery; but the perfumer is the artist who finds a way to utilize the invention. Often a perfumer possessing an artistic taste and the skill of blending also possesses sufficient knowledge of chemistry to appreciate and understand the newest chemical products of perfumery and their uses.

The so-called toilet preparations, creams, lotions, etc., are manufactured by distinct chemical methods which must be worked out by chemists. This, however, is not true of the blending of odors with which to scent these preparations.

The knowledge of chemistry is not absolutely essential to the perfumer so long as he has artistic taste for odors, is a student, and has a fine sense of odor;

but, with the aid of the chemist manufacturing the product, he can become a celebrated perfumer.

Perfumery is an art and a science. To appreciate the depth of the study and the time it takes for development, it will be sufficient to state that there are not many real perfumery chemists and perfumers in the world.

Hygiene

Although perfumery and flavors have played an important and interesting role in the history of the world and although even in our present civilization they are playing important roles in our daily life, some refer to perfumes and other scented products as articles of luxury only. To consider perfumery from this viewpoint would be misleading and erroneous, to say the least.

Because of their antiseptic and germicidal qualities the very essential oils and chemical products used in perfumery are of great benefit to our health. Aromatic chemical substances and oils used in the flavoring of our food, aside from their pleasant taste, act as preservatives, as without them it would be impossible to store the foods which we so much enjoy. Of course, strong chemical preservatives could be used; some, however, might be injurious to health. Cloves, cinnamon, cardamom, pepper, etc., are spices containing certain essential oils. It is because of these oils that the taste is agreeable and our foods are so preserved as to make them safer for shipment and more readily marketable.

The antiseptic qualities of essential oils have been known for a great many years. In determining the power or quality of an antiseptic, phenol (carbolic acid) is taken as a unit and therefore the phenol co-

efficient is the usual determining factor of the strength and quality of antiseptics.

		Phenol Coefficient
Citral	The substance contained in lemon and orange oil as well as in cheap lemon grass oil. By this is meant that citral is sixteen times as strong an antiseptic as carbolic acid	16
Eugenol	The principal ingredient of oil of cloves. It is because of the presence of eugenol that oil of cloves is used as a deadener of pain in case of toothache. Having such high phenol coefficient and possessing an agreeable taste, it can be readily seen why clove buds are used in the making of savory sauces	15
Thymol	One of the best known antiseptics used for throat and mouth lotions and toothpaste. Recently several processes have been developed to manufacture thymol synthetically	25
Menthol	Previously mentioned as contained in peppermint oil	19
Menthone	Also contained in peppermint oil; sometimes used as a flavor in perfume	10
Citronellol	One of the principal ingredients of rose perfumes, also contained in rose oil	14
Ionone	The well-known violet substance made from citral.	1.75
Methyl salicylate, or oil of wintergreen	Chemically made of salicylic acid. This product has been used for many years as a flavor, as a drug, as an anti-rheumatic for internal and external use	5
Thujone	Contained in a great many essential oils	12
Artificial musk	Used for the blending of perfumes	4
Heliotropin	A chemical heliotrope product	3
Thymene	Contained in various essential oils	8
Safrol	Contained in oil of sassafras	11
Acetophenone or hypnone	Used as a drug, as a hypnotic and a perfume in new-mown hay odors	4

As a matter of fact, there are very few essential oils and chemical products used in perfumery which are of less germicidal or bacteria-killing value than phenol. Very often its bacteria-killing power is increased, sometimes doubled, by the addition of alcohol. This is mainly due to the solvent action of alcohol, which dissolves the oil and makes it easier of absorption. Alcohol of 60 to 80 per cent strength

is a strong antiseptic; less than 60 and more than 80 per cent are less effective. As most perfumes are alcoholic, it can be seen that the germicidal action of essential oils and chemical products is increased to a great extent by the alcohol used.

Other chemically made perfume materials—as for instance benzyl cinnamate and other cinnamates, some of which are contained in balsam Peru, used for the healing of wounds—are much stronger in their bacteria-killing powers than those previously mentioned. Some of these possess great wound-healing properties. Most all of the perfumery materials and flavors are, chemically speaking, aromatic substances and as such are very strong germicides. Some of the cinnamates have been found valuable in the treatment of consumption. This phenomenon is being further investigated.

Possibly, the actual benefit derived from the use of perfumery substances and flavors is beyond our comprehension. The truth is that no one will think of applying such things as carbolic acid to his face or body. Perfume materials, on the other hand, are used constantly and freely, seemingly for the pleasure it gives one, but actually for the benefit derived therefrom. Barber shops and other similar places would be subject to danger of contagion, were it not for the fact that perfume materials are applied constantly. The habit of kissing would be more dangerous if it were not for the use of mouth and tooth preparations containing such powerful antiseptics as thymol, menthol, etc., which have fifteen to twenty-five times the germicidal and antiseptic value of carbolic acid.

In view of this, can it not be truly said that perfumers and manufacturers of flavoring materials used in our everyday life, instead of being creators of arti-

cles of luxury, are in fact benefactors to our present generation?

Relation between Taste and Smell

As taste and smell are very closely related, perfumery and flavors were taken up together. It is to be remembered that slight colds, throat ailments, diseases of the nose, and even faulty teeth affect the taste to a considerable extent. The same is true of smell.

It is also a question of development, memory, and training, however, but unless a person has a keen sense of smell and taste to start with, there is no chance for development. As far as memory goes, unless the expert whose business it is to pass on perfumery and flavoring substances is trained to remember how previous samples tasted or smelled, he is not in a position to become very efficient.

Some people have developed taste and smell to a point where they not only distinguish the quality of an odor, but find most minute quantities of foreign substances present. As a matter of fact, the nose and the tongue are considered just as sensitive as the finest chemical reactions. A product might be considered pure and still contain most minute quantities of foreign substances which may be recognized by a trained nose.

It is strange that human beings differ in taste and smell development. Animals, on the other hand, if of the same class, usually possess the same power of taste and smell. As far as humans are concerned, studies have brought out most peculiar facts. Girls, for instance, have a finer sense of taste than boys for things that are bitter. On the other hand, boys have a finer sense of taste for things that are sweet.

The taste of chemical products and their relationship to one another have not been fully investigated. There are supposed to be approximately one hundred and fifty thousand organic chemicals, each one possessing a different taste, if not odor. Of these, quite a number have been investigated. Solid products are usually almost tasteless, but as soon as they are dissolved, a taste is developed. The following facts are interesting:

		Parts
Quinine, when dissolved can be recognized	1 in	39,000
(Children have been known to recognize it)	1 in	300,000
Sugar	1 in	199
Salt	1 in	2,240
Strychnine, ordinarily considered not much more bitter than quinine	1 in	4,000,000
Nicotine, a product present in tobacco	1 in	15,000,000
(Owing to use of tobacco and liquor, in course of time the fine taste is depressed.)		

Odors have been investigated along similar lines, and it has been found that certain ones are recognizable from a great distance in proportions from 1 in 5000 up to 1 in 250,000, depending upon the product investigated and the speed used. Some persons are supposed to be able to distinguish the odor of hydrocyanic acid (prussic acid) 1 in 2,000,000. Time given for the recognition of the odor is very often figured down to a thousandth of a second.

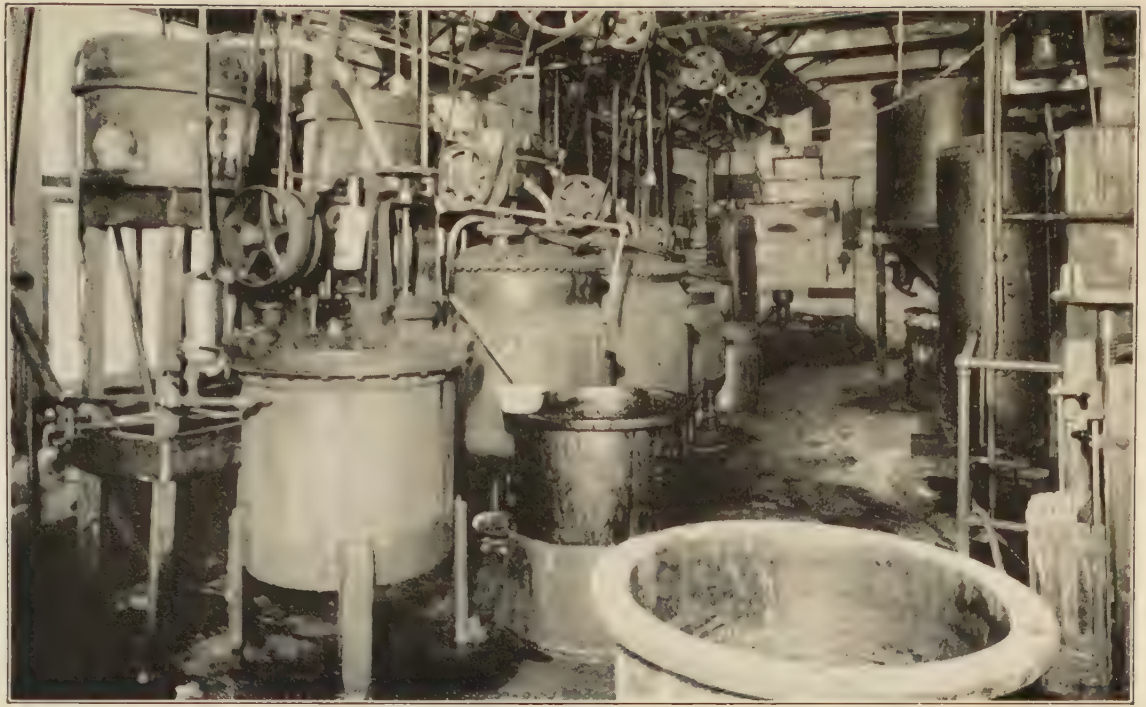
The sense of smell is possibly the finest sense possessed by the human being and its close connection with taste can be easily demonstrated. If one closes his nostrils he will not be able to distinguish many tastes. For instance, vinegar, hydrochloric acid, nitric acid, phosphoric acid, and butyric acid are said to taste alike if the nostrils are held absolutely tight. We know that each one of these chemical substances has a different taste and smell. If under the conditions described above no difference can be detected, it can

be readily seen that taste depends a great deal on odor. Without the sense of smell only the qualities of sweet, sour, salty, and bitter can be well defined, and the really fine points of taste are lost.

Past Accomplishments and Future Development

So far as the perfume industry itself is concerned, one might say that the field of the essential oil and flower product as obtained from natural sources has been thoroughly investigated and therefore ought to be considered exhausted. Chemists realized some years ago that the future of the perfumery industry would have to depend entirely on the synthetic perfume chemistry for its supply of raw materials. It is a fact that new creations in the field of perfumery cannot be built up without the aid of the chemist. The history of the past thirty or forty years is therefore most interesting.

When the chemist first ventured into the field of perfumery, he was considered a nuisance. In the first place, people had very little faith in chemistry and were afraid that products chemically made would have a detrimental effect on the perfume or flavor. This made commercial progress very difficult for the chemist. As a matter of fact, propaganda was carried on by manufacturers of natural perfumery products who remembered how the growers of madder root (natural alizarin) were put out of business following the discoveries of Graebe and Liebermann, who found a way to make it chemically; also how the growers of indigo in India were put out of business by the discovery of Adolf Bayer, who showed the chemical constitution of indigo and later produced it synthetically. For these reasons they were afraid the chemist entering the field



Courtesy, Van Dyk and Company.

A Department of a Jersey City, N. J., Plant Manufacturing Perfumery Chemicals.

of perfumery was also going to rob them of their livelihood. Therefore the flower growers and producers of natural perfumery substances made it a point to discourage the use of chemical perfume materials; but the chemist in his great desire to investigate and search new fields was not to be discouraged and eventually succeeded in overcoming the prejudice and false propaganda.

The production of vanillin by Tiemann and Wallach in 1872 and the discovery of coumarin by Perkin in 1875, and of heliotropin, a heliotrope-smelling substance contained in pepper, by Eykman and Poleck in 1885, blazed the way for the chemist to win confidence and get a solid footing in this industry. Terpineol, a substance made from turpentine and having an odor of lilac, was produced by the French chemists Deville, Bouchardol, and Voiry in 1887. This together with the inventions of artificial musk and ionone made it possible for the chemist to make real headway in this field; but even at that, although the perfumer realized the great assistance received by the work of the chemist, harmful propaganda still continued, and succeeded in beclouding the issue until a few years ago. It is surprising, but true, that, while all perfumers must and do use chemical materials in the production of their perfumes, and while the producer of flower products has long given up the fight against the chemist and the use of chemicals, a number of manufacturers lack the nerve to tell their customers that modern perfumes cannot be made without the use of chemical products, and are still trying to keep from the public the fact that their perfumes are created by the skill of the chemist and the art of the perfumer, who is the blender and creator of the modern perfume.

The chemist, starting with something definite in

mind, first investigated the chemical compounds found in nature. This being accomplished, he manufactured the various products chemically and combined them in accordance with his findings. Later, however, he discovered that products of different chemical constitution, not belonging to the same class as the products found in nature, gave similar odors. This is the discovery really responsible for the great successes in perfumery. These chemical substances, which are not related to the natural substances at all, are much more powerful, more lasting, and more desired by the public than the natural substances.

Up to the time that the chemist found these new substances, true odors of the violet, lilac, lily, narcissus, and carnation types were unobtainable, as the extraction of the perfume from these natural flowers gives poor or no results.

The latest of these new chemical materials is a lily or lilac product made from an ill-smelling substance contained in Java citronella oil. Within the past few years the perfumer has found out how to use this product successfully, so that today practically every new bouquet and flower odor, other than rose and violet, contains some of this new substance called hydroxy citronellal.

The great growth of the perfume industry in the world is the result of the discoveries made by the chemist. In this country, for instance, in 1914 the production of perfume and perfume materials was valued at about sixteen million dollars; in 1924, in accordance with census returns it is about eighty-five million dollars, or an increase of over 400 per cent. Our experts alone for the year 1923 amounted to almost seven million dollars.

Had the chemist not entered this field, the growth

would have been impossible. Furthermore, there would have been no possibility of procuring natural raw materials had there been a demand for them, as France could not have increased its production 1000 per cent or more. As to whether other countries could have helped in supplying these flower products, that is an open question.

Within the past two years an association of the American perfumers has set aside a sum of money for an investigation as to whether flowers such as roses, jasmines, tuberoses, etc., could be successfully grown in California. The task is not an impossible one. To the writer's mind roses grown in Oregon and California have a better odor than those grown in France. The same is true of violets and jasmine flowers grown in certain parts of the United States.

Whether or not this investigation is going to be successful remains to be seen, but the American perfumer should be congratulated for this effort. The real obstacle seems to be the matter of cost, labor being the principal element of production of the flower products in France. On the other hand, inasmuch as America has the chemical raw materials and brains and chemistry does not have to depend upon rain or sunshine and other climatic conditions, there is no reason for any country to surpass it in this field.

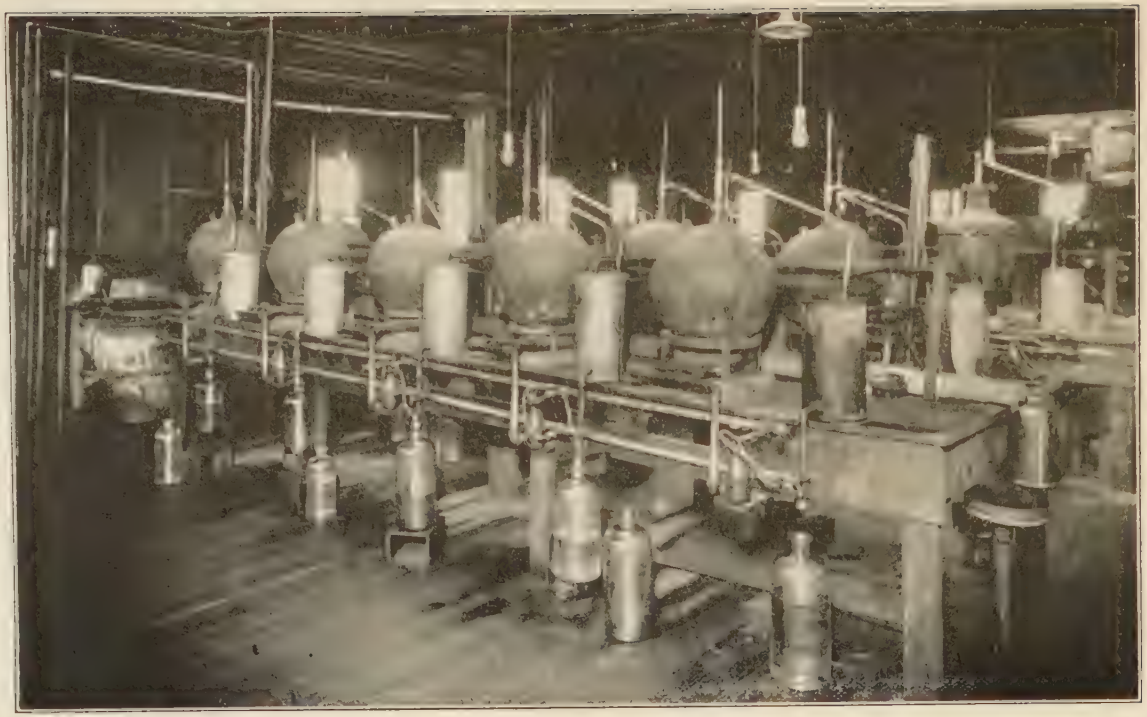
In connection with the further development of perfumery and flavors, there are a great many problems still to be solved—e.g., vanilla, the well-known flavor which is extracted from vanilla beans growing chiefly in Mexico and the Bourbon Island. The principal odor of the vanilla fruit, or bean, as it is called, is due to vanillin. Vanilla bean contains from 2 to 4 per cent of vanillin, but there are other desirable substances in

the vanilla bean which, up to the present time, have not been chemically produced.

Occasionally there is a shortage in the vanilla crop or the growers come to an understanding and raise prices. To illustrate, vanilla bean, which sold around three to four dollars about a year ago, is not only difficult to procure, but is now selling at twelve dollars a pound, or three times as much. If it were not for the manufacture of chemical vanillin, which is conducted in this country on a very large scale, our national flavor, vanilla, would have become a great luxury. But vanillin has its disadvantages. If combined with the bean, it improves the flavor, but without the bean it stands neither the heat of baking nor freezing temperatures as required in the manufacture of ice cream. It is hoped that the chemist will soon produce a flavoring substance to combine with vanillin in order to make it more stable.

Other flavors for household use which it is hoped will be developed soon are the fine aroma of the strawberry, raspberry, and other similar fruits. The actual flavoring materials contained in these fruits are almost immeasurable. Fruits are composed principally of water and pulp, and while aromatic chemicals contained in them are numerous, the quantities are very small. This is one of the reasons why flavors contained in fruits have not been so thoroughly investigated as other similar chemical materials. As a matter of fact, very often most of the flavor is in the rind or peel of the fruit and not in the fruit itself.

At the Bureau of Chemistry of the Department of Agriculture, Washington, D. C., scientists have been spending a great deal of time investigating flavors contained in apples, pears, and a number of other fruits. As it takes carloads of fruit to get a measur-



Courtesy, Van Dyk and Company.

Vacuum Distillation of Expensive Perfumery Chemicals in a Jersey City, N. J., Plant.

able quantity of flavor, it must be realized that the job is tedious and time-consuming.

A complete investigation has been made of apples. It is peculiar that the malic acid contained in apples is also contained in a great variety of fruits not related to apples at all. Certain artificial fruit flavors on the market today are mixtures composed mostly of ethereal products and are not very satisfactory or very agreeable. A better grade of flavors is extracted from the fresh or dried fruit by means of a solvent to which certain aromatic oils are often added. Unfortunately, these extracted flavors are not strong enough, neither do they possess all of the aroma contained in the natural fruit when freshly picked. Therefore, since a part of the fine aroma is lost in the process, certain additions are usually made to fortify these natural extractions.

It is hoped that single chemical bodies reproducing the exact aroma of the fruit will soon be made on a commercial basis, thereby aiding the manufacture of suitable fruit flavors of this type. Since this has been accomplished in the perfumery field, there is no reason why similar results should not be obtained in the creation of fruit flavors. During certain times of the year and in certain climates, fresh fruits are unobtainable, but if the chemist does find new chemical substances to reproduce or improve the odor and flavor of the fruit, flavors containing the aroma of the fresh fruit will be obtainable at all seasons of the year. The problems of jasmine, tuberose, and farnesol are still unsolved.

In the perfumery field new chemical products are produced continually, but single chemical substances are still missing for the creation of the true odor of the jasmine flower. The odor of jasmine, as produced

artificially, is accomplished by combining certain known products contained in the natural flower. The number of chemical products found in natural jasmine up to the present time is about twelve, but this number is not complete. Artificial or synthetic jasmine is being manufactured and consumed in very large quantities, but speaking frankly, the jasmines so produced do not completely replace the odor of the product extracted from the flower.

As far as the tuberose is concerned, the natural product as extracted from the flower is very unsatisfactory. The synthetic chemical product built up is still less satisfactory. A strange phenomenon is that perfume cannot be properly extracted by any known method from such strong-smelling flowers as tuberose, hyacinth, narcissus, lily of the valley, lilac, or even carnation. Unfortunately, in the case of tuberose, not having a satisfactory chemical substitute, its natural product must be used, whether good or bad.

A chemical substance, tuberone, is considered to be the leading note of the tuberose odor. It has been produced on a small scale chemically, but on account of impurities it is not considered satisfactory.

A chemical substance called farnesol is contained in very minute quantities in different flower products. Farnesol has been recently synthesized. The manufacture of pure farnesol on a commercial basis would complete several perfumes and odors. Farnesol is present in tuberose, cassia, jasmine, ylang-ylang, etc.

As far as chemical flower products are concerned, the list is fairly complete. The field is a fertile one for the production of new products not known at present, and there is no doubt that chemists all over the civilized world even at this moment are constantly giving their attention to the development of aromatic chemical sub-

stances suitable for the building up of new perfumes and flavors.

Products which today are known as perfumes and solvents, tomorrow may become very important drugs. Processes and chemical steps used in the building up of fine perfumery substances are producing valuable drugs for the relief of pain and the curing of diseases. The most powerful germ-killing antiseptics produced to safeguard the nations of the world against contagious diseases and infections are closely connected with the perfumery field. It can be authoritively stated that tuberculosis is today being aided by the help of a chemical product used in perfumery.

In view of these accomplishments, it is hoped that the chemist, instead of relinquishing his hold on this industry, will continue his work with greater vigor than before. There is a great deal to be done and the chemist can be depended upon to solve the problems of health, industry, and the preservation of our natural resources.

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CHAPTER XVII

THE PETROLEUM INDUSTRY

GERALD L. WENDT

Assistant Director of Research, Standard Oil Company (Indiana)

Since the transcontinental railroads were built seventy years ago nothing has caused such a change in both the city life and country life of America as the development of the automobile. Not long ago the best residential district of our cities was close to the business streets, but now these fine old homes are used as tenements and the home districts are in the suburbs, often many miles from town but just as accessible by automobile as the former region was on foot. So, in the old days, farm life was lonesome, full of hard work, and the trip to town took a whole day and was the event of a month. Nowadays the farmer can drive many miles to deliver his milk and purchase supplies and yet be back in time to do more work that day with the aid of a tractor than he formerly did in several days. Perhaps in the evening the whole family drives to town again to attend the movies. All this change has been possible because of the automobile and because this country has been blessed with an enormous supply of petroleum oil. But petroleum added to the comforts of life long before the automobile was invented, for the kerosene lamp was a distinct improvement for comfort and pleasure over the candles that lighted the evenings in George Washington's

day. And even in the use of candles people are thankful for the cheaper and better candles that come from paraffin wax as compared with the old tallow or sperm candles.

More important than all of these is the fact that petroleum is practically the only source for the manufacture of lubricating oils and this age of machinery would be impossible if there were no oil to permit the wheels to move. No application of power, whether it be windmill, water power, electricity, or steam, is possible without oil or grease as lubricant. There are hundreds of different lubricating oils. Some of these are very light as, for instance, those used in a watch; others are very heavy and thick to enable them to withstand high pressure and high temperature, such as those used in locomotives or steamboat engines.

Some of the less well-known products of petroleum are also important. Instances of these are the oil that is used to soften wool before it can be woven, the colorless medicinal oils and vaseline, and finally, the asphalts and heavy oils that are used for road oil or fuel oil. This brief list can only suggest the importance of the petroleum industry in American life today.

Origin of Petroleum

The word "petroleum" comes from the Latin words "*petra*" and "*oleum*," meaning "rock oil." This oil occurs in tremendous quantities hidden beneath the surface of the earth, just as coal is, and its history is much like that of coal. It is easy to see in a lump of coal the remains of prehistoric plants, ferns, and tree trunks, which have been changed by the chemical action of heat and pressure through thousands of years until only the primary chemical constituents are left,

namely, carbon and hydrogen. The same processes, acting on other vegetable remains under water and also on the bodies of fishes and other marine animals, have caused a somewhat different method of decomposition which, instead of leaving a solid residue of carbon, left a liquid mixture of many different compounds of carbon with hydrogen known as hydrocarbons. And just as coal deposits have usually been protected by a layer of shale, which is merely hard baked mud or clay, so the oil was absorbed in heavy beds of shale or of porous sand and was prevented from escaping by the deposit above it of limestone or shale. In this way great pools of oil, holding millions of barrels, have been preserved for our use far beneath the surface of the earth. Some of them are not far down; in fact, petroleum was first obtained from wells which had been sunk in the search for water. In a region where oil is known to be present, however, wells have been drilled to a depth of nearly a mile and a half in order to tap successive pools of oil lying one beneath the other with shale and rock layers in between.

Petroleum was originally an American product. For more than a century seepage of oil from the earth has been known in northwestern Pennsylvania and southeastern New York State. In 1849 a druggist in Pittsburgh collected the oil from a brine well in Tarentum, Pennsylvania, and sold it at fifty cents for a half-pint bottle as "A Natural Remedy! Celebrated for its wonderful curative powers." In 1854 the Pennsylvania Rock Oil Company was organized and submitted a sample of the Pennsylvania petroleum to the famous chemist, Professor Benjamin Silliman of Yale University, who analyzed it and showed that the various products in it could be used as illuminating oils, lubricat-

ing oils, and oils for making gas. In 1859, at Titusville, Pennsylvania, the first well was dug by the superintendent of this company, Colonel E. L. Drake, who devised methods for drilling that are still in use. An oil pool was found seventy feet below the surface and oil was pumped out at the rate of about fifteen barrels a day. During the next few years many wells were drilled in this region so that the Oil Creek region in Pennsylvania fairly bristled with the drilling derricks. That State continued to be the leading oil field for many years. During the last decade of the past century much oil was obtained from Ohio and Indiana; during the first ten years of the twentieth century the great Midcontinent field in Oklahoma and northern Texas was developed; and in recent years production has been heavy on the Gulf Coast of Texas, in California, and in Wyoming.

The Pipe Line

Petroleum was at first very costly because of the expense of drilling and pumping but especially because it was expensive to transport the oil for many miles in tank wagons or railroad tank cars from the wells to the refineries and again for long distances to the cities where it was marketed. The great development which gave us cheap petroleum was that of the pipe line. Nowadays oil is pumped from the well through large pipe lines directly to the refineries which may be thousands of miles away. Refineries on the Atlantic Coast and on the Great Lakes are now connected by pipe line with all the great oil fields east of the Rocky Mountains so that they can obtain oil cheaply from almost any part of the country. The low cost of pipeline transportation is largely responsible for the rela-

tive cheapness of petroleum and therefore of its products. When the oil reaches the seashore or the lakes it is refined and the resulting products are sent to the ends of the earth by means of great tank steamers which carry many thousands of barrels in one cargo, and thus make kerosene, for instance, as common in China as it is in America.

Refining

The first step in refining crude petroleum is to separate its various constituents by the process of distillation. Since petroleum consists almost entirely of chemical compounds composed only of carbon and hydrogen, which are therefore called hydrocarbons, all parts of it are much alike chemically. The chief difference between the various hydrocarbons is in the size of the chemical molecules. The smallest molecules present contain only one atom of carbon combined with four of hydrogen and thus have the chemical formula CH_4. This is a gas known as methane or marsh gas which is dissolved in the crude oil and separates from it on very gentle heating. Together with it, especially as the temperature rises, comes ethane, C_2H_6, which is also a gas. As the temperature is slowly raised, one after another of the hydrocarbons which compose the oil reach their boiling point and pass off as vapor. When the true gases, such as methane and ethane, have been removed the next class that distils off consists of the very light liquids whose boiling point is only slightly above ordinary temperature. In this class are pentane, C_5H_{12}, and hexane, C_6H_{14}. These light and very volatile liquids are used for solvents in the rubber and varnish industries, and are usually called naphthas. Some of them go into gasoline but

the gasoline fraction also contains heavier molecules with as many as nine or ten carbon atoms as, for instance, decane, $C_{10}H_{22}$. By this time the temperature of the still has reached about 400° Fahrenheit and the boiling points of the compounds that are obtained by further heating the still are too high to permit their use in gasoline. As the temperature rises, therefore, the next fraction obtained is used for burning in lamps that are fed by means of a wick. In this fraction, which is kerosene, are compounds with ten to fifteen carbon atoms in the molecule. Now, as these light compounds are removed from the still by boiling, the temperature slowly rises and the residue in the still becomes increasingly higher in specific gravity and more viscous. The distillation is, however, continued until temperatures well above 700° Fahrenheit are reached. The other fractions obtained are gas, oil, light paraffin distillate, and heavy paraffin distillate. The last two contain paraffin wax and are the chief sources of lubricating oils. After the paraffin distillates have been removed, the residue in the still is a thick, black liquid which may be sold directly as asphalt or as fuel but it is often heated still further, in which case it decomposes and forms a layer of coke in the still. This coke is very porous, light in weight, and since it was formed entirely from hydrocarbons, it contains practically no mineral matter and therefore burns without leaving an ash. When carefully made it is so pure that it can be employed directly for the manufacture of graphite electrodes for use in electric furnaces.

In this way crude petroleum is separated into seven or eight major fractions. Midcontinent petroleum will furnish about 4 per cent of gas, 25 per cent of gasoline and naphthas, 15 per cent of kerosene, 40 per cent of

gas oil, 12 per cent of paraffin and lubricating oils, and 4 per cent of coke. The gas may be used for fuel in the refinery or may be sold for illuminating purposes. The coke can also be sold directly for domestic fuel or for industrial purposes. The other four fractions require further refining before they can be sold. The gasoline must be purified and perhaps separated into special naphthas; the kerosene must be chemically treated so that it will burn cleanly in lamps; the paraffin distillates must be chilled to take out the wax; and the remaining oil must be manufactured into hundreds of different kinds of lubricating oils for special purposes. The large gas oil fraction containing 40 per cent of the original crude oil is too viscous to burn well in lamps and yet too thin to have lubricating value. It is, therefore, converted by special processes into lighter oils, chiefly gasoline.

Cracking

In 1923 over seven billion gallons of gasoline were required to operate the fourteen million automobiles which are now in use in the United States. This enormous quantity could not be produced directly from the available crude petroleum if only the 25 per cent of gasoline which is originally present were used. If we were limited to this original gasoline there would be a shortage, and its price would be much higher than it is. The fact that cheap gasoline is available is therefore due largely to a process for manufacturing gasoline from the relatively useless gas oil. This process for chemically manufacturing gasoline from heavier oils was devised in 1912 by chemists of the Standard Oil Company of Indiana, and is known as cracking. It imitates somewhat the conditions under which petro-

leum oil is stored beneath the earth's surface; that is the oil is kept for many hours at a high temperature and is prevented from boiling by holding it under pressure. If the temperature of the oil is above 700° Fahrenheit, the large molecules are so violently agitated by the heat that they break up into smaller ones. Thus the hydrocarbon, $C_{20}H_{42}$, which is present in gas oil, breaks up into two molecules which contain ten carbon atoms each, or perhaps into three molecules of six or seven carbon atoms. In this way a molecule which formerly boiled at so high a temperature that it belonged to the gas-oil fraction is now broken up into several molecules which are suitable for gasoline. This is the essential process that is known as cracking and that has added so much to our gasoline supply and, therefore, to the usefulness of the automobile.

In practice the process consists in running several hundred barrels of gas oil, or other heavy oil, into a still that has been built to withstand a high internal pressure. Fire is applied but boiling does not take place at the usual temperature because the still is kept tightly closed to build up pressure. The boiling point of any liquid is, of course, the temperature at which its own tendency to evaporate, which is technically called the vapor pressure, becomes slightly greater than the pressure of the atmosphere. The vapors are therefore able to push the atmosphere aside and the liquid is seen to be actively boiling. If the pressure of the atmosphere is increased mechanically, boiling does not take place until a higher temperature is reached, when the increased vapor pressure is again able to push aside the atmosphere. In cracking stills, the pressure is kept close to one hundred pounds per square inch. This is enough to prevent the gas oil from boiling at any temperature which is reached by

the still. On the other hand, if the gas oil molecules crack or break up into gasoline molecules these smaller ones are at a temperature which is above their boiling point, even under a pressure of one hundred pounds. The gasoline is, therefore, able to boil off, while the gas oil remains in the still. When the temperature is maintained for hours above 700° Fahrenheit, there is a slow formation of gasoline, which immediately vaporizes and passes out of the still into the condenser where it is cooled and collected as a liquid. The same process can, of course, be used for the manufacture of gasoline from kerosene, the only difference being that pressures well above one hundred pounds must be used to prevent the boiling of the kerosene itself. Until fifteen years ago kerosene was the most important product of petroleum, and gasoline was a rather undesirable by-product. Today, however, it is gasoline which is in greatest demand, and there are some refineries which actually manufacture it from kerosene. By this process of cracking, the production of gasoline from petroleum can be doubled. That is, the gas oil can be made to furnish as much gasoline as was originally present in the crude oil. This chemical process of cracking is therefore one of the major factors in petroleum refining.

Casinghead Gasoline

A small quantity of gasoline is also obtained from natural gas. Much of this gas comes from petroleum wells where the gas separates from the oil by coming to the earth's surface when the natural pressure is released. It is, therefore, saturated with gasoline vapor which can be removed from it, either by compressing it, which liquefies the gasoline, or by passing it over charcoal, which absorbs the gasoline out of

the gas. This gasoline from natural gas is called casinghead, or natural gasoline, because it is drawn from the casinghead of the oil well. It is very light and low boiling and is mixed with ordinary gasoline, especially when a very volatile or low boiling gasoline is desired. Such a gasoline is known as high test gasoline and since it boils more easily than the usual gasoline, it is used under conditions of low temperature, such as are encountered by airplanes or by automobiles in cold regions.

Purification

All these varieties of gasoline require chemical purification. There are three types of impurities which must be removed. The least important and most easily removed are the compounds which give the crude gasoline a very unpleasant odor. The smell of crude gasoline is due to hydrogen sulfide and to similar organic compounds. These are removed by washing the gasoline with an alkaline lead solution, made by dissolving litharge, lead oxide, PbO, in strong sodium hydroxide solution. The lead reacts with the sulfides and precipitates as lead sulfide, and an oil of sweet odor is thus produced. Only very small quantities of these evil-smelling compounds are present, and while they do no great harm in the engine they must be removed before the gasoline can be sold.

The second class of impurities consists of the colored compounds. These also are harmless in themselves but must be removed before the oil can be sold, since a clean, colorless product is demanded by the trade. This demand is correct because the process of removing the colored compounds also removes other compounds that tend to deposit sticky or gummy materials

in the storage system or in the carburetor. A colorless gasoline is therefore assurance that the oil has been carefully treated to remove such harmful compounds. This treatment consists in scrubbing the oil thoroughly with concentrated sulfuric acid, which reacts with the colored and gum-forming constituents so that the final product is both sweet-smelling and colorless.

The third class of impurities consists of the sulfur compounds, which have neither color nor odor but are distinctly harmful because when they are burned in the engine they first form sulfur dioxide and then sulfuric acid. This acid would collect in the crank case and would cause serious corrosion of the engine. The sulfur compounds, however, are removed by the same treatment with sulfuric acid that has been described previously. The final stage in the treatment consists in washing out the acid and the alkali with large quantities of water. The gasoline is then ready for the final stage in the refining.

Now that the impurities have been removed, the gasoline is once more distilled, this time by the use of steam. The crude gasoline is run into a steam still and steam is passed through it, thus causing it to boil out of the still. It passes through what is known as a fractionating tower, which is so built that all the constituents whose boiling points are too high to permit their use in gasoline are condensed in the tower and are returned to the still. Thus the product that cools and condenses as a liquid in the condenser is a sweet-smelling, colorless oil of the right specific gravity and boiling points to serve as a fuel in the automobile engine. The control of the boiling points is the most important part in this stage of the process. A good gasoline requires a definite mixture of boiling points, so that there is enough low-boiling material present to evapo-

rate readily and thus start the engine easily, and so that there is also enough high-boiling material present to furnish the necessary power and mileage. Most of the gasoline boils between 200° and 380° Fahrenheit, with small proportions both above and below these figures. The boiling points, or the distillation range of the gasoline, are continually tested at the refineries in order to insure a proper product and one uniform in composition at all times.

Other Petroleum Products

The processes used for most of the other products of petroleum are similar to those for gasoline. They are separated from each other by careful distillation and are purified by sulfuric acid and alkali, or by percolation through absorbent clay for decolorizing, and are carefully inspected in the chemical laboratory at every process of manufacture. The manufacture of kerosene is almost identical with that of gasoline except that higher temperatures must be used in the stills. The equipment employed in the plant is therefore somewhat different. The lubricating oils are also separated into light and heavy fractions by distillation and are purified with equal care. Special machinery must often be used. The waxes, for instance, are solid and must be separated from the oil after they have crystallized at a low temperature by filtering the oil through large, cold filter presses. When the crude wax has thus been obtained it is separated into fractions of various melting points by a process known as sweating in which partial melting is used for separation, just as partial boiling is used in distillation. Thus, paraffin waxes of various melting points are produced which are used for different pur-

poses, such as sealing fruit jars, candles, waxed wrapping paper and drinking cups. The waxy material known as vaseline is separated by a still different process. Almost all of these are purified by the use of sulfuric acid and some products, such as the perfectly colorless medicinal oils, are treated with large quantities of very strong acid to make them colorless. It is impossible within the present space limitations to discuss the manufacture of all of these products, but the scope of the work and the great importance of the various chemical processes should be evident from the examples given. From the time the oil reaches the refinery until it is stored in great tanks of finished products, it requires close attention and the skill of good chemists to insure the proper operation of the manufacturing processes.

While the general method of petroleum refining is about the same as was recommended by Professor Silliman seventy years ago, improvements are constantly being made and the industry faces many problems which the chemist has not been able to solve. There are, for instance, literally thousands of patents issued on improvements and detailed modifications of the cracking process. Although the fundamental reaction of cracking is the same in all of them, it is produced by different methods and they must be carefully studied from such points of view as the amount of gasoline produced per gallon of heavy oil, the amount produced per hour in a still, or per pound of coal as fuel, the amount of labor required to operate them, the expense of the installation, and its safety of operation, etc. Some of the very important problems would be overlooked by a man not familiar with the petroleum industry. An instance of this is the loss of gasoline that occurs when the oil is stored in tanks. All tanks lose

some oil by evaporation because they cannot be made absolutely gas tight, and therefore the tank breathes out gasoline vapor during the day as it is warmed by the sun, and breathes in fresh air without that gasoline when it is cooled at night. If a tank contains three million gallons of gasoline, which is not unusual, and loses one per cent of this on standing for a month, the loss is thirty thousand gallons which, at twenty cents a gallon, is six thousand dollars per month. To be sure, losses are seldom as high as one per cent in modern steel tanks, but this figure shows how a small and apparently negligible item may cause serious financial losses. No method has yet been devised for entirely preventing this loss, but there are a number of devices in use which have reduced it to an almost negligible quantity.

Some By-Products

Then there are many chemical problems dealing chiefly with the utilization of the by-products from refining. When sulfuric acid reacts with undesirable compounds in oil it produces a thick, pasty sludge which would seem to be entirely useless except perhaps as fuel. It is actually used, however, after some further treatment, for the manufacture of asphalt which is employed both for road building and for making asphalted roofing materials. Some of the gases formed in the stills are carefully refined and are used to manufacture several valuable but fairly rare chemicals such as isopropyl alcohol. This is one of the few instances of a chemically pure product produced from petroleum.

The possibility of petroleum being used as a source for many organic chemicals and even for the manufacture of foodstuffs has often been emphasized. Fifty

years ago coal tar, which is obtained when coal is distilled for the manufacture of illuminating gas, was also a very cheap product used only as fuel or as road oil. Today, however, it is the source of many high-class products, such as dyes, perfumes, and drugs. This great development has come through chemical research, and there are many who predict that the day will come when chemical research will transform petroleum, which is now used chiefly as fuel, into an infinite variety of useful substances. They point out that while coal tar can furnish aromatic compounds, it has no aliphatic constituents, though petroleum is almost entirely aliphatic. Now it is the aliphatic compounds which comprise cellulose and vegetable materials, fats and proteins, which are the chief constituents of the animal body, and finally carbohydrates which, with fats and proteins, comprise the three great classes of foodstuffs. There is, indeed, no theoretical obstacle to the manufacture of butter or lard, sugar or starch, and even the proteins, from the compounds which are present in petroleum. Perhaps it will some day be done but there are three great practical difficulties. One is that petroleum consists of many thousand distinct compounds, very similar to each other, which are hard to separate completely. Another is that these oils are chemically very unreactive, as is shown, for instance, by the fact that they can be purified with concentrated sulfuric acid without affecting anything but the undesirable impurities. It is therefore difficult to convert them into other compounds, such as sugar. The third and perhaps fundamental reason is that the science of chemistry has not yet developed to the point where chemists know how to do these things and the chemical geniuses who must yet

discover the way by hard work in research are few and far between.

There is one problem which stares the petroleum chemist in the face, and that is the question as to what we shall do when the supply of petroleum oil gives out. Our common life is now so thoroughly organized on the basis of the automobile which must have oil fuel, and on machinery which must be lubricated, that there is no longer any chance of going back to the good old days when industry was practically unknown. On the other hand, government scientists have estimated that all the known sources of petroleum will be exhausted within twenty years, so that most of those who read this book may live to see the day. New pools of oil will be discovered and perhaps the day that we are wondering about is still far off, but ultimately the time will come when the petroleum age is over.

Oil Shale

Probably the first recourse of the chemist of that day will be to develop the vast deposits of the rock known as oil shale. There are in Colorado and Utah whole mountains of this rock and in the State of Indiana alone there are more than 450 billion tons of it. It is saturated with a solid, organic material, called kerogen, which is a peculiar asphalt-like or wax-like material that is changed into oil when heated. These shales will produce from ten to fifty gallons of oil per ton, so they can ultimately furnish even more gasoline than the deposits of petroleum, but the expense of mining, crushing, and heating these many tons of useless rock is so high that shale oil cannot at the present time compete with petroleum. Its use will, therefore,

probably be postponed until our petroleum resources have been exhausted.

Meantime there are other possibilities. Alcohol is an excellent motor fuel in many respects, though it furnishes only two-thirds as much power per gallon as does gasoline. It can be produced not only from grains and sugars but from several vegetable waste matters, such as sawdust from soft woods. The process is not used now because it is more expensive than the production of gasoline, and in any case the supply of waste material is now too small to supply more than a fraction of the fuel needed. Before gasoline begins to fail, chemists will probably have devised methods for the manufacture of alcohol from other agricultural wastes, such as straw, corn, and sugar cane stalks, leaves, etc.

Future Research

The need for chemical research will be sufficiently obvious from this discussion of the major problems of the future in this field. There are numberless other important questions which need to be answered. The very vital science of lubrication is itself still an infant. We do not know just how an oil reduces the friction between two metallic surfaces. We do not know why an oil adheres to a metal even against great pressure and scraping action. If there is an especial attraction between the metal and the oil we do not know what compounds are most attracted by the metal nor under what circumstances. In the same way, the chemist will have much to say in the design of better automotive engines, for there are still many questions as to exactly what goes on when the explosion takes place in the cylinder; that is, how the explosion starts, just what is responsible for passing the reaction on from

one molecule to the next, and how the reaction rate can be influenced so that the explosion delivers its power smoothly at the right time and place.

Summing up, then, the petroleum industry is among the very largest in the country, both in size and in importance. Its development has been rapid and refining methods have been developed which are efficient and are the products of the highest chemical skill. Nevertheless, from the chemical point of view a very great development is still certain and the next generation will see improvements or revolutions of which we do not now even dream.

CHAPTER XVIII

PHOTOGRAPHY, OR PICTURE MAKING BY LIGHT

S. E. Sheppard

Assistant Director, Research Laboratory, Eastman Kodak Company

Many chemical arts date back to the beginnings of human history, but photography is essentially a product of eighteenth century discovery and nineteenth century invention. Some one with a sharper eye than his or her fellows might have noticed very early the possibilities that lay in the darkening and bleaching actions of light upon colored fabrics or pigments. Although Vitruvius and Pliny, two Roman writers of the early Christian era, did observe these changes with painters' colors, their only comment was to recommend those which were more stable. It was not until 1727 that Johann Heinrich Schulze definitely recorded that silver nitrate mixed with chalk was darkened by light, and made stencil pictures on this mixture. In three years' time, therefore, it would be fitting to celebrate the bicentennial of photography.

Now, it is well worthy of attention that the optical side of photography was invented much earlier; namely, in the period roughly described as the "Renaissance of Learning." Among a multitude of other inventions Leonarda da Vinci (1452-1519) described in his manuscripts a combination of a dark chamber (*camera obscura*) and a pinhole by which a real image of an external scene could be thrown upon a flat sur-

face. However, the first published description was by Batista della Porta in 1558, while the earliest mention of a camera with a lens is by another Italian, Daniello Barbaro, in 1568. Although the camera was ready, it had to wait more than two hundred years before chemistry began to find means of fixing the images obtainable. Soon after Schulze, Scheele in Sweden, and Thomas Wedgewood, son of the famous potter, were experimenting on the darkening of silver salts by light, the Swede showed that silver chloride, so-called horn silver, was reduced to the metal, and the Englishman began the "Copying of Paintings upon Glass and of Making Profiles by the Agency of Light by Nitrate of Silver" (1790-1802). This article was published jointly by Wedgewood and Sir Humphrey Davy. It is curious to note that Davy, already a great chemist, failed to obtain any means of dissolving out unchanged silver salt and of really fixing the photographic image.

For practical purposes this early photography had two great drawbacks: First, no means of fixing the image were known; and second, the process was very slow. Some thirty years later (1834-1835) Fox Talbot conceived independently the idea of photography and improved greatly upon Wedgewood's leather and sheets of paper washed in water. He then found if he washed paper with a weak solution of common salt (sodium chloride), and bathed it in a strong solution of silver nitrate, he could obtain a much more rapid and uniform blackening in light than with either silver nitrate or silver chloride alone. Any one may repeat Talbot's experiments by taking the following solutions and using them as prescribed:

Make up a solution of common salt, 450 grains in 2

pounds of water. Soak the paper in this for a few minutes and then dry. Then prepare a solution of 60 grains of silver nitrate to 1 ounce of water, float the paper on the surface of this solution so that one side of the paper is well saturated, and then dry in darkness. This whole operation should be carried out in a yellow light. Now, place a stencil or any cut out design over a sheet of this paper and expose to daylight until thoroughly dark and then wash in a strong solution of common salt, followed by a rinse with water. A copy of the design will be obtained in the manner of the first photographers.

Talbot discovered, therefore, the sensitizing action of soluble silver salts upon silver chloride, a fact which is still used in the making of printing-out papers. Moreover, he discovered that strong solutions of common salt (sodium chloride) would dissolve out the unchanged silver chloride and fix his pictures. In 1835 he was getting direct pictures in a camera in about ten minutes in very bright light.

Although Talbot must rightly be considered the father of photography, the work of Niépce and Daguerre demands notice. Nicéphore de Niépce (1765-1833) wished to save lithographers the work of copying designs upon the stones. He found that a natural asphalt "bitumen of Judea" which is soluble in oils, such as oil of lavender, become insoluble when exposed to light. Thus, after printing under a line drawing on to a metal plate covered with this asphalt, the unprotected parts, that is, the lines, could be dissolved away. He then "etched" these lines out with a bath of acid and thus produced the original of all photomechanical printing or reproduction processes.

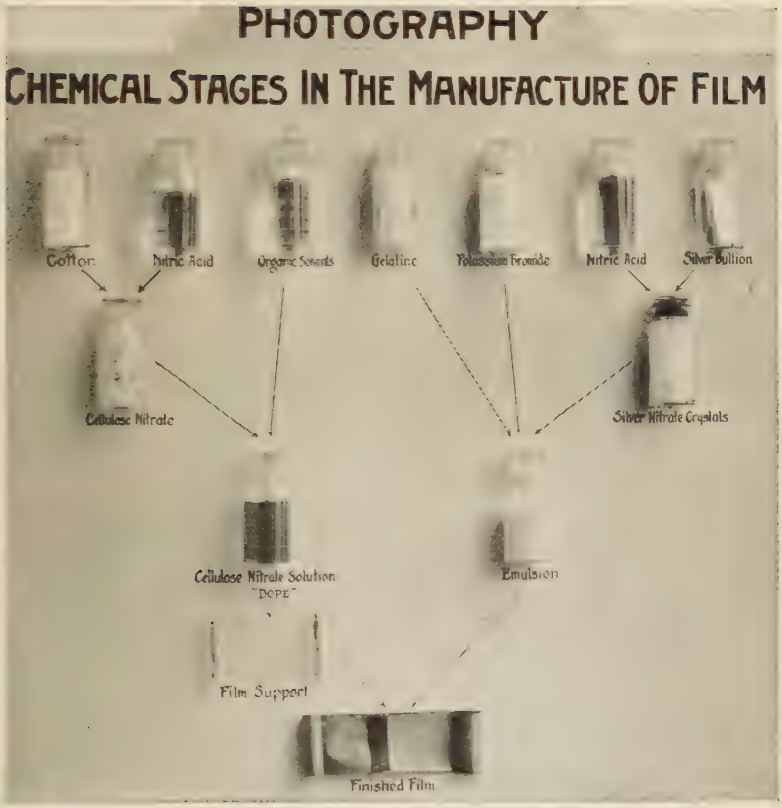
The Daguerreotype

Niépce went into partnership with another Frenchman, Daguerre. The latter was a theatrical scene painter who used a camera to help in his work. He wished to fix the images he obtained with his camera and this brought him into relation with Niépce. It was Daguerre, however, who discovered the "latent image." He used to treat polished silver plates with the fumes of iodine, thus obtaining a surface of silver iodide, very thin, and with the silver itself hardly covered. Exposures to light were very long; in fact, taking many hours to obtain an image. One day, it being very cloudy, he put away a plate after a brief exposure with the idea of trying again in better light. What was his astonishment on taking the plate from the cupboard to find a beautiful picture of the scene on which it was previously exposed! He tried again putting a briefly exposed plate in the mysterious cupboard and was again rewarded. Upon investigation the benevolent fairy was found to be metallic mercury or quicksilver, the fumes of which condensed upon the invisible or latent image.

Daguerre used hypo (thiosulfate of soda), which was discovered by Herschel in 1819, to dissolve away the unaffected silver iodide. The image after development with mercury vapor was made more permanent by gilding, that is, toning the volatile mercury compound with metallic gold. Daguerreotypes were very beautiful and caused much interest and enthusiasm, yet they represent a straying from the main path of photography; as has been said, "Daguerreotype died in the same year as its inventor," 1851—but the idea of a latent or invisible but developable image was all-important.

In 1841 Fox Talbot discovered independently the possibility of developing a latent image upon his calotype or Talbot-type papers. In this process the paper was impregnated with silver iodide; then, before placing in the camera it was washed with a mixture of silver nitrate and gallic acid (made from oak galls). Talbot found that such paper showed after a brief exposure little or no image, but on bathing it in more of the gallic acid and silver solution and then warming, an image appeared and ultimately became dense black. This process was patented by Talbot, and by it he obtained a hundredfold increase of sensitiveness; he was able to reduce his exposures from one hour to half a minute. It was Talbot who realized the possibility of printing positives from negatives (1844), although these names were introduced by Sir John Herschel in 1841. This production of negatives from which many positives and duplicates can be obtained was a great advance as compared with the Daguerreotype.

Before looking more closely into the ways of the chemist in modern photography what does this amount to? It is fair to say that the invention and development of photography is comparable with that of printing. Printing multiplied at will the symbols which stand for words, just as words, when arranged in sentences, express our thoughts; but before the word comes the fact to which it refers. Now, it will be remembered that the earliest writing was picture writing such as that of the Egyptians, the Chinese, and the Aztecs; also, it may be remembered that these pictures gradually acquired a purely conventional meaning. They were made in a quick and convenient manner and became more and more like shorthand signs.



Courtesy, Eastman Kodak Company.

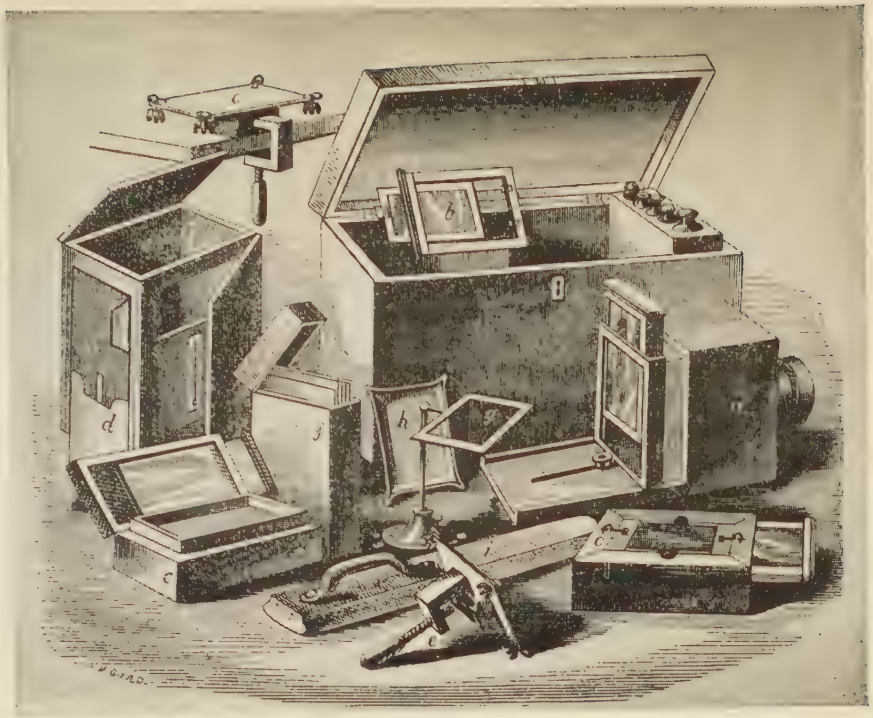
Modern Picture Writing

Now, photography and, above all, cinematography, provides a fuller picture writing, a method of direct representation of fact and action. Without this invention it may be said that our complicated civilization would be almost dumb and half blind. Imagine for a moment our world with all photographic processes removed; journals, books, magazines would be bereft of illustrations other than those given by the beautiful but tedious processes of making wood cuts, hand engravings, and lithographs. There would be no halftones and no rotogravures. The engineer and the business man would have no blue prints, no photostats, but only tracings and mimeographs. It is difficult, if not impossible, to name any phase of human activity in which photography does not now play an important or even essential part. The engineer, the explorer, the surveyor, whether on foot or in the air, needs it at every turn. In medicine and in surgery the utility of photography increases every day. It is the handmaid of all the sciences and recent advances dealing with the architecture of crystals, the structure of atoms and of molecules were made largely by its aid. In the preface to a recent work occurs the following: "It is probably not too much to say that the most definite advances in scientific investigation made in recent years have proceeded from the application of photography." ("Photography as a Scientific Implement," Collective Work, 1923.) Artists may not always praise photography, but they admit that "without photography one half the world would not know what the other half was doing in art."

This memorizing of our life by pictures to an extent undreamed of by our forefathers is raised to higher

powers in cinematography. With motion almost life itself is breathed into these images. The commercial and dramatic advances of cinematography have been rapid, and the movies are now recognized as second only, if that, to the newspapers in affecting public opinion; although technically this development is still in an early stage, it is possible to look ahead at coming changes. Amateur cinematography brings it into the home, and the portfolio of snapshots will in time join the family album of past days. In the movies themselves we shall have color (color cinematography); concurrent speech and music (speaking pictures); plastic depth (stereomovies); all these will make the illusion more complete. Moreover, we are only forecasting direct developments. It is the nature of inventions first to pursue individual lines; then, to influence each other, and, finally, to be joined together in new advances. Electric telegraphy meant quick transmission of words to any distance by a code, as in the Morse code; telephony meant sending speech itself, while radio has eliminated the wires. We are already seeing the practical beginnings of wired and even wireless transmission of photographs, examples of which have recently been shown by C. Francis Jenkins of Washington. These things foretell the beginnings of radio-movies in the home and perhaps even of tele-vision; that means that one day it will not only be possible to call up a friend three thousand miles away and speak to him but to see him at the same time.

This may seem fantastic but not more than modern photography and modern radio would have seemed from the viewpoint of the eighteenth century. Let me emphasize here that it is probably the chemist who will have to solve these problems. Chemists often have



Courtesy, Eastman Kodak Company.

The Portable Equipment Required for Photography in the Days of Wet Plates.

to answer the questions which only physicists can properly ask; the camera was a physical question to which the answer was the photochemically sensitive silver emulsion. There are physical questions being asked now to which the chemical answer has not yet been made.

The Wet Plate

So much has been done, however, that we may well return to actualities. The first pictures made by Talbot were on paper. The paper let the image sink in and was not satisfactorily transparent for making a negative. An improvement was made in 1848 by Niépce de Saint-Victor, a nephew of the older Niépce. He used a film of albumin or egg white on a sheet of glass to hold up the sensitive substance, which in his case was silver iodide. The same year saw the introduction of collodion to hold the sensitive salt. Collodion forms a transparent film; it is made by dissolving nitrated cellulose in a mixture of grain alcohol and ethyl ether and is well known for its use in covering skin cuts and abrasions. We shall have more to say of nitrated cellulose directly. Scott Archer applied it instead of albumin on glass, and the wet plate process of photography held the field from 1850 to 1880. The collodion contained soluble iodide with some bromide. After coating, while still moist or jelly-like, it was sensitized with a solution of silver nitrate, which formed a nearly invisible layer of iodobromide in the film. It had to be exposed while still wet and was developed immediately after exposure with an acidified solution of either ferrous sulfate (sulfate of iron made by dissolving metallic iron in sulfuric acid) or of pyrogallic acid. This latter substance is obtained from gallic acid by distillation, in which process it

loses a molecule of water. The wet plate process forced a photographer to carry on his back the whole factory for the production of photographic material. The illustration shows what might be termed a photographic factory of this period.

Somewhat later dry collodion plates were introduced, but the tendency of collodion to become hard and horny made these of uncertain value. Modern dry plates and films were due to the introduction of gelatin by Maddox in 1871 to replace collodion and to the discovery of alkaline development by Russell in 1865. In the wet-plate process there is always an excess of soluble silver salt (silver nitrate), and it is necessary to prevent the developer from working too powerfully and running the silver on exposed and unexposed portions alike.

What is a developer? It is a reducing substance; that is, one which removes metals from combination and precipitates them. In general, reducing agents are greedy for oxygen and reduce more strongly; that is, are oxidized the more easily, the more alkaline or the less acid the solution is. Alkaline development is only possible with the silver halides (the compounds of silver with chlorine, bromine, and iodine are termed silver halides; chlorine, bromine, and iodine, being termed the halogens or salt formers) which have no excess of silver salt present, but if anything an excess of alkaline halide. Such development is sometimes called chemical while the acid development is called physical; but this distinction is unreal since the same essential chemical reaction occurs in both cases. In the gelatin silver dry plate there are a multitude of microscopically small silver bromide particles suspended in gelatin. In ordinary negative emulsions the silver bromide will form about 30 per cent of the total

Courtesy, Eastman Kodak Company

The Manufacture of Pure Silver Nitrate.

weight. These particles are actually crystals of microscopic, and even less than microscopically visible, size. In negative emulsions they may attain a diameter of 2μ or 3μ (8/100,000 to 12/100,000 inch), while in positive emulsions they will not exceed 0.1–0.2μ and are, indeed, largely colloidal. To make such an emulsion we must first have very pure silver nitrate. This is manufactured by dissolving ingots of silver in strong nitric acid, a process carried out in large porcelain dishes to avoid contamination. The silver nitrate is then recrystallized, dissolved in water, and added carefully to a solution of pure potassium bromide together with a little iodide of potash, the solution containing some gelatin. If no gelatin were present, the precipitate of silver bromide or iodobromide would lump together and fall to the bottom of the vessel, but the gelatin keeps it spread out, whence the term "emulsion" is derived. On a manufacturing scale this operation is carried out in large silver-lined vessels heated outside with steam and provided with silver-plated agitators. More gelatin is stirred in, bringing the strength up to about 7 or 8 per cent. The soluble salts formed by the reaction must now be washed out from this emulsion. To do this it is chilled to a jelly, then shredded by being pressed through holes, and the vermicelli-like strands are washed in cold water. To prevent the jelly from absorbing too much water, this is hardened; for example, with calcium sulfate, because water containing calcium and magnesium salts does not swell gelatin as much as soft water. The shredded emulsion is then melted and coated; that is, spread uniformly on the support. This support may be glass or celluloid film or paper.

Flexible Films

The introduction of flexible celluloid film support was due to George Eastman and was an advance as great as that of gelatin in emulsions. It not only made the light-weight roll and the pack film possible but also the cinematograph. This celluloid film is made like collodion from nitrated cotton, and production involves a series of interesting chemical operations. The cotton, usually linters or waste from the textile industry, is carefully purified by treatment with solutions of alkali, bleaching with chlorine, and washing. The bales are then put through a drier, which breaks them up and dries the loosened material. The dry cotton passes onto a nitrator; this may be a large pot with an agitator, or a centrifugal machine. Here the cotton is immersed in a suitable mixture of strong nitric and sulfuric acids. Nitration does not destroy the fibrous structure of the cotton but alters this chemically. The excess acid is whirled off centrifugally and the last traces are removed by very thorough washing. Then the water is removed not by drying but by displacement with grain or amyl alcohol, liquids which do not attack the cellulose nitrate. This also is done in centrifuges so that only a certain amount of alcohol is retained. The nitrated cotton is then transferred to dissolvers—big rotary mixers in which it is stirred in organic solvents. These are usually methyl compounds, such as methyl alcohol to which certain amounts of higher boiling solvents may be added. The solution is not like a solution of salt; it is thick and honey-like and is termed "dope." It is then filtered under great pressure to remove undissolved specks and fibers and is ready to coat. The dope is furnished in large drums to the coating ma-

Courtesy, Eastman Kodak Company.

Apparatus for the Manufacture of Emulsion.

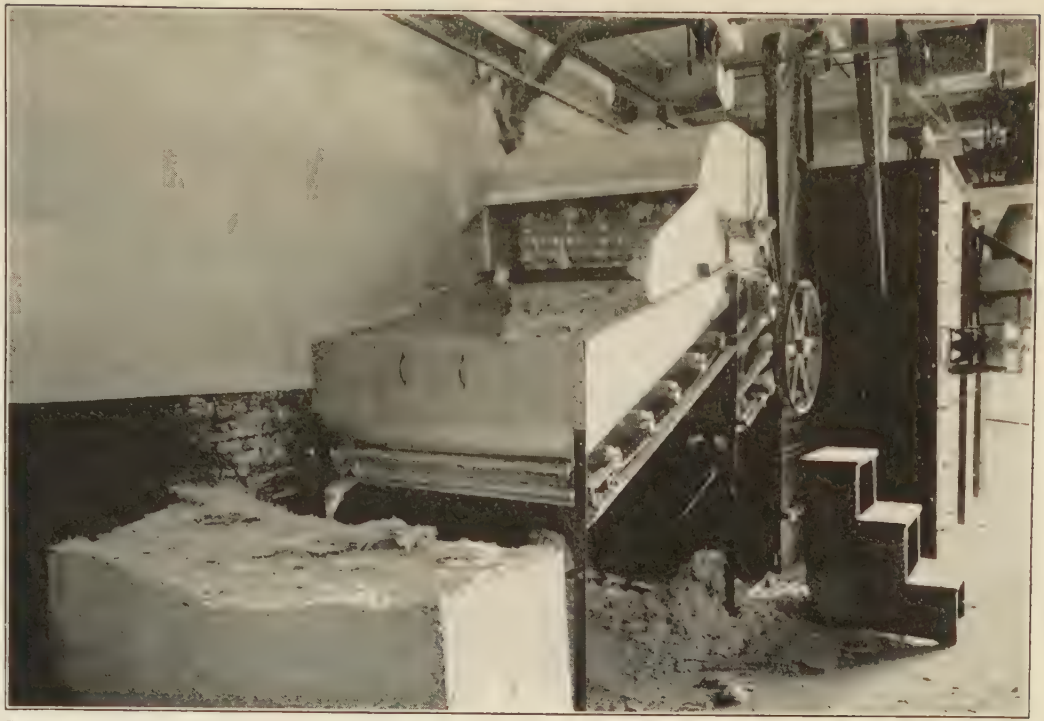
chines, the chief feature of which is huge slowly rotating wheels of polished metal. The sticky mass is spread on these, dried, and rolled up as an even transparent film of about 5/1000 of an inch thickness.

The other two supports for photographic emulsions are glass and paper; glass is not usually manufactured as a part of the photographic industry but paper may be. However, the chemistry of paper making is a story in itself; it must suffice to state that the manufacture of photographic paper demands the utmost in skill and in purity of materials. The sensitive photographic emulsion is like the princess in the fairy tale; it has the ability to detect a rose leaf beneath a dozen mattresses; in other words, the very least impurities that would never otherwise be noticed. On one or other of these supports the emulsion is coated, an operation which has to be carried out in a dim, religious light—yellow or orange or deep red or even faint green. The amount of light which may be used and its color depend upon two things—the total sensitivity to light of the emulsion, and its color sensitivity. Generally emulsions for making negatives are much more sensitive than those for making positives but also all the silver halides, while sensitive to violet and blue light, are nearly insensitive to green, yellow, and red light. Chemists have found that these colors can be made chemically active by faintly dyeing the silver halides with certain aniline dyes. At first it was possible to sensitize for only the green and yellow but later dyes were discovered which make the plates sensitive to the whole spectrum or "panchromatic" (all colored). The importance of these sensitizing dyes is out of all proportion to the quantity made or to their direct selling value. Before the World War they were exclusively made in Germany as part of its great and won-

derfully organized industry of synthetic organic chemicals. When the war came, supplies were cut off and color sensitive plates were imperative for military photography by airplane, as well as for many more peaceable uses. American and British chemists had to hustle to make their own sensitizing dyes, and their work has thrown much light on the constitution of this class of dyes besides adding to their number, so that now they are made in this country as well as abroad. Although used in very small quantities they have very big names, which are shortened for practical purposes; thus, one of them, ethyl red for short, is properly called diethylisocyanine iodide. Other dyes are available in photography for making light filters; these are sheets of dyed gelatin used to cut down the strength of certain rays either in dark room lamps or in taking pictures. On the other hand, dyes are used in color photography to replace the silver of the developed image and give colored pictures. This, however, is getting rather ahead of our story.

Developers

Another photographic product of the organic chemical industry is organic developers. It is true that one of these, pyrogallic acid or pyrogallol, is made from natural sources, but most of them are synthetic products occurring as intermediates of the dye industry. These are made from benzene, the light oil obtained on first distillation of coal tar. They are made from benzene or occasionally naphthalene by replacing hydrogen atoms either by two hydroxyl groups or two amido groups or one hydroxyl and one amido group, placed in the molecule in a certain way. What are hydroxyl and amido groups? If we take a hydro-



Courtesy, Eastman Kodak Company.

A Drier for Cotton after Purification and before Nitration in the Manufacture of Film.

gen atom out of a water molecule, we have a hydroxyl group. Do the same to an ammonia molecule, and we have an amido group.

A Chemical Camel

Speaking of developers brings us to development, but this requires first a word about gelatin. Gelatin is perhaps the most abused and almost the most useful material in photography. It is a sort of chemical camel carrying water through the desert, doing what nothing else can, and yet full of tricks and disturbing uncertainties. As you know, gelatin can be obtained by stewing bones, but photographic gelatin is usually made from calfskin. The skins are soaked in lime water, which removes fat and hair and plumps the hide. Then the hide is extracted with hot water, the resulting jelly spread out thin, and dried. Gelatin swells in plain water up to six or seven times its bulk, but in weakly alkaline acid baths very much more. Sudden changes from alkaline acid baths, from strong solutions of salts to weak, from hot to cold, make gelatin very irritable. It may soften, may melt or wrinkle, or, if coated on a support, it may strip away. A chemist can go on working with gelatin for a lifetime and learn something new every day. If he dissolves a little to a dilute solution and treats it with chemicals, he may conclude it is quite mild-mannered, although acting either as a weak base or a weak acid, but if he deals with it in large quantities in different batches and treats it roughly, then he will get quite another opinion. Some day an inspired photochemist is going to give gelatin a final push into the ice cream can; or generally relegate it to the culinary arts. He is going to make super-ultrasensitive plates on silver

mirrors, like Daguerre only better, and print off positives and negatives at will by photoelectric contact processes besides getting all the color he wants through interference; but not yet a while. For the present he will have to toil along with dyes and gelatins—and trouble.

The part played by gelatin is of importance because the developing solution has to diffuse through it and swell it. This diffusion takes place almost as easily as in water. The developer will be made up of an organic reducing agent and alkali; for example, washing soda (carbonate of soda) to speed it up and sulfite of soda. This latter chemical acts as a preservative; that is, it lessens the oxidation of the reducing agent by air and prevents stain. Sometimes a small amount of bromide of potash is added. This acts as a restrainer or slows things down, behaving in photographic development therefore somewhat as it does on the human organism. A good developer knows which silver bromide grains have been struck by light; it takes the bromine away and leaves the silver behind. The silver bromide grains which have not been struck by light it leaves severely alone, although be it noted that such grains may be made developable by other agencies than light such as friction and certain chemicals. The developed film, plate, or paper is fixed in hypo solution. Hypo, properly called thiosulfate of soda, can be made by heating sulfur and sulfite of soda together but is usually manufactured by oxidizing sulfide of soda, a by-product of the alkali industry. If a negative is too dense, it can be thinned or reduced by treatment with certain silver-dissolving chemicals. Ferricyanide of potash (made by roasting hoofs and horns with iron salts), together with hypo, forms one reducer; another is ammonium persulfate, which is ob-

Courtesy, Eastman Kodak Company.

Nitrating Cotton in Film Manufacture.

tained by oxidizing sulfate of ammonia, a gas works by-product, electrolytically. If the negative is too thin, resort may be had to intensification. The silver is bleached with bichloride of mercury (corrosive sublimate, used by people desirous of an uncomfortable death, also as an antiseptic) to a silver chloride and mercurous chloride (common calomel, somewhat less harmful and used in liver pills). This bleached image is then blackened either with ammonia or with a developing solution.

The development and fixation of positives is much the same chemically as that of negatives. We think of photographic operations as being carried out in large or small trays or tanks, but in the finishing or processing of motion picture film considerable advances beyond this have been made in what is known as continuous or automatic processing. The handling of the great quantities of cinematograph film used in the production of pictures was formerly carried out by winding the film around a rack or frame and processing this in a series of deep tanks. For drying it was wound on huge open-work drums like squirrel cages, and these were rotated until the film was dry. For greater economy of space and labor more mechanical methods are now used. In these, the film is run through a series of vertical tubes, in one system up to 40 feet in height, which contain first the developer, then rinse water, fixing bath, and then wash water. It then goes on through a drying cabinet, through which purified and heated air is passed, in opposite direction from the moving film. It is a long step from the one-man photographic factory of early days to that of modern times. The great variety of photographic products necessary for the world-wide extension of the art demands that a great manufacturing industry be main-

tained. It is not surprising to learn, therefore, that the output of motion picture films in the United States alone has exceeded 65 million feet in a month or 150,000 miles a year—more than enough to go around the world five times. To make this uses up some 5 million pounds of cotton per year, millions of pounds of gelatin, and over 3 tons of solid silver every week, which is one-twelfth of all the silver mined in the United States each year.

We have now followed the whole chemistry of making a finished photographic film, and the accompanying chart shows in brief the chemical stages in the manufacture.

CHAPTER XIX

SYNTHETIC RESINS

A Chemical Contribution to Structural Materials

A. V. H. Mory
Associate Director of Research, Bakelite Corporation

Introduction

When it was first shown that the building up of organic compounds from inorganic, and even from the elements themselves, was not necessarily a vital process, i.e., peculiar to living organisms, even men of science were startled. Since that day we have come to regard the building up, or, as we say, the synthesis, of any compound whatever, whether of animal or of vegetable origin, as representing a legitimate if not a promising problem for chemical research. And so it is that many of the products of Nature's laboratory may now be produced from cheaper products in a laboratory of man's making. Formerly it seemed almost lacking in proper respect for Dame Nature, if one presumed to imitate her in her wonderful creative processes, but such has been the advance in the domain of chemical synthesis that we are no longer content merely to imitate Nature but now often surpass her in her unaided creative effort.

In a stricter sense, of course, it is Nature that does it all. Left to herself, however, she fashions her handiwork to meet the age-long needs of her children and has no interest in man's twentieth century desires.

Nevertheless, she works most faithfully for anyone who understands her ways and is willing to provide suitable harness. Chemistry and the chemical laboratory represent man's effort to learn Nature's innermost impulses, and when they are found to be in harmony with man's desires, industrial processes and equipment are forthcoming to harness Nature for man's service.

Thus, today, we find Nature forced out of her regular habits and guided in the preparation of many products pleasing to man's present-day desires and needs —products surpassing, for man's special requirements, anything produced by Nature for her own special needs.

Today, to mention only a few of the many examples that might be given, we have colors of far greater value to man than any produced by Nature unaided, synthetic organic medicinals more efficacious than Nature's herbs afford, and synthetic resins in certain particulars far surpassing the natural resins. It is to these last named that brief consideration is invited.

The Invention

There are many substances which may be led to form noncrystalline, resinous bodies, either by polymerization (a sort of self-combining process), or by interaction and condensation of two or more substances, or by a combination of these processes. Notable among such resin-forming substances are phenolic bodies and aldehydes, of which ordinary phenol (carbolic acid) and formaldehyde are, respectively, the best known representatives.

This reaction of phenols and aldehydes has long been known, having been studied by the German chem-

ist, Bayer, in 1872. For years following this, one investigator after another sought to produce an artificial resin of commercial value, but without noteworthy success. The phenol-aldehyde reaction in their hands yielded only inferior products—products either somewhat similar to ordinary resin and unable to compete with it in price, or bodies that were porous and so resistant to all attempts at modification as to be of no practical use. It remained for the American chemist, Baekeland, to bring the reaction under the control necessary to produce a resin of superior properties and of wide industrial value. It was in 1909 that he announced the results of his work, protected his invention by letters patent, and the name of his new product by copyright.

Since then synthetic resins have been the subject of much research, but thus far results of importance have been confined largely to further developments along the lines first laid down by Baekeland. Thus, considering the brief space here allotted us, we shall do well to give consideration to the industrially important phenol-formaldehyde products (known to the public under the copyrighted names, Bakelite, Redmanol, and Condensite) to the exclusion of others which are mainly of scientific interest.

The materials employed, viz., phenol and formaldehyde, will naturally be thought of as two very unpromising raw materials from which to produce such an odorless, tasteless, and inert body as results under proper conditions from their interaction—but such are the wonders of chemistry.

Process of Manufacture

The process by which this synthetic resin is produced is, briefly, as follows:

Phenol and a solution of formaldehyde, in reacting proportions, are put into a steam-jacketed kettle, and heat is gradually applied. Soon the materials begin to react and, in doing so, to liberate heat. So intense may the reaction become with rise in temperature that the steam must at times be shut off and cold water circulated in the jacket to keep the process from proceeding too far or the materials from boiling out of the kettle.

After a few hours of heating, the contents of the kettle will be found to have separated into two layers —the heavy, melted resin in the bottom and water on top. The water having been removed, the melted resin is allowed to run from the kettle into shallow pans to cool.

All this sounds simple, and it is, but success depends on a selection of just the right conditions, involving a number of factors. Any other set of conditions may be depended on to produce a resin of different, and, more than likely, indifferent character.

Properties of Product

But let us now give attention to the properties of the resin produced under favorable conditions—the resin that has just been left to cool in the pans.

First, we note that it is a clear substance, somewhat resembling amber in appearance, but as brittle as ordinary rosin; and, like rosin, easily melted, and soluble in alcohol and other solvents. But herein lies the difference that has made this synthetic resin superior for many uses to any of the natural resins, not excluding amber: When the natural resins are heated they melt, solidify on cooling, and may be heated and melted again and again without much change in their

fusibility or solubility. The synthetic resin, on the other hand, when prepared under proper and well-known conditions of time and temperature, and with suitable proportions of the reacting substances, changes, with application of sufficient heat, from a molten to a solid resin that can no longer be melted by any heat up to a temperature of 500° Fahrenheit, when charring begins. Furthermore, this same "curing" by heat renders the resin insoluble in all the ordinary solvents, and causes a remarkable increase in strength.

In the process of this change to the strong, infusible, insoluble state, some gas is given off, which, under ordinary conditions, causes the mass to swell. Such a hard, infusible, insoluble, spongy mass was obtained by one of the early investigators, who gave up the fight at this point. The most important procedure in Baekeland's invention was that of applying pressure along with the heat, thus producing the first solid, clear, strong, hard, amber-like, synthetic resin now so well known as a material for pipe bits, beads, etc.

Industrial Uses

But let us go back to the brittle, fusible, soluble resin in the cooling pans, and, now that we know something of its wonderful property of "freezing" in the heat that first melts it, let us see if we cannot find industrial uses that have been waiting for a material of just such properties. The first field that suggests itself is that of protective coatings for metals and other materials that are changed by exposure to the air. With the aid of suitable solvents, it should be easily possible to apply a thin coating, which, on drying and baking, should give a most durable protective

film. Expectation has been justified by experience. Such solutions have found useful application as lacquers for brass and other easily tarnished metals.

We should expect also to be able to prepare cements that would be useful at temperatures causing certain others to fail. Here, again, we are not to be disappointed, as witness our electric lamps whose glass-bulbs are securely imbedded in their metal bases by a cement, the principal binding substance of which is this same phenol-formaldehyde resin.

But a far greater field and one that promptly suggests itself is that of plastic molding. In a class by itself, and still of great value among natural resins, is shellac, a resin of more than ordinary strength and toughness, much used in electrical insulation, and very serviceable in this way at ordinary temperatures. At higher temperatures, however, it softens and further heating does not greatly alter it in this regard. An insulating substance was, therefore, greatly to be desired which, after flowing freely when heated in the molding operation, would promptly set, even while still hot, to a strong, rigid solid that would not soften when again heated. Such an ideal substance was to be found in the new phenol-formaldehyde resin, and its entrance into plastic molding has been rapid. Being unusually strong, rigid, and inert in its finished state, it is taking the place of metal, porcelain, wood and other structural materials for a number of mechanical uses. Since it also possesses high insulating value, its advent into the electrical field filled a long-felt want. In no other industry, in fact, has it found such extensive use.

But we are getting a little ahead of our story. Baekeland found that the initial pure resin alone was not suited to molding, for, when melted, it was too fluid to

work well as a plastic, it shrank too much on cooling, and the finished product shattered too easily from a blow. These difficulties he overcame by impregnating finely ground fibrous materials with the resin in its first, uncured state, and carefully controlling the process of impregnation so as to get just the right degree of plasticity for proper flow in the mold. Such molding preparations, employing finely ground wood flour or asbestos as the fibrous ingredient, today furnish the raw material for molding an almost endless number and variety of articles of commerce.

In the field of electric insulation the introduction of phenol-formaldehyde resin as a molding material is the one big event since the discovery of hard rubber vulcanization—also an American triumph. For many uses, the synthetic resin has supplanted this other valuable insulating material, because of superior rigidity and greater resistance to change from heat and exposure, amounting practically to permanence under all ordinary conditions. Another great advantage lies in the saving of labor made possible by the fact that metal parts can be firmly imbedded during the molding operation; also since the material faithfully copies every detail of the mold, even to its polish, it was possible to dispense largely with subsequent work, as well as the assembling and finishing. This enabled the new resin to effect savings in spite of its higher cost.

Laminated Forms

Another important field that has been developed is that of the so-called laminated forms. Here, the original, uncured resin is the basic substance, and paper or cloth are the materials impregnated. For this purpose a varnish is prepared by dissolving the

uncured resin in alcohol, and the paper or cloth is passed through this varnish and then dried. In practice, long rolls are treated in one continuous operation, the sheet being rolled off at one end, passed through a bath of the varnish, then through a drier, and the dried sheet rolled up at the other end. This dry, saturated sheet is then cut into uniform lengths, which are piled one piece upon another in a steam-heated, powerful hydraulic plate press. The pile of sheets is submitted to a pressure of many tons and a temperature sufficient to cause the resin first to flow freely, blending the sheets into one compact whole, and then to solidify, binding them strongly and permanently.

These laminated forms have found extensive use in both the electrical and mechanical fields. They are found on the market as Bakelite Dilecto, Formica, Celoron, Textolite, Micarta, Fibros, etc. As a material for radio panels, the laminated paper is well known. As a material for silent gears, the laminated cloth is finding extensive use, having the advantages over raw hide of not being affected by oils or dampness, and not being a food for rodents.

Thus, through chemical research, has the industrial world come into possession of a new material with new and valuable properties and constantly widening application.

A list of the articles into whose manufacture it enters, or even of the industries it serves, would be too long to be included here, but no treatment of the subject would be at all adequate which failed in some fashion to indicate the extent of its use. The list of individual industries not only embraces those classed as electrical and mechanical, but extends even to the jewelry trade. The manufacturers of radio apparatus

found the material waiting for them when the new means of communication and entertainment burst overnight on a surprised and appreciative public, and they are today among its largest users. It is also of interest that there is not an automobile on the road today which does not employ some part whose essential material is phenol-formaldehyde resin—in timing gear, ignition and lighting systems, radiator cap, lever ball, spot light, and horn.

A more recent development is the use of the synthetic resin as a binder in the manufacture of grinding wheels. Its strength and rigidity, maintained in spite of the heat generated in grinding, make possible greatly increased speed and efficiency in the grinding operation.

In jewelry we find the pure resin, plain, vari-colored, or clouded, rivaling the beauty of precious stones. A high refractive index makes for brilliancy, and a warm "feel" for comfort in such use. As a substitute for amber, in smokers' articles, its use is evidenced in the window of almost any dispenser of these wares.

Chemical Properties

The mere fact that any one substance should find such varied use makes a study of its chemical properties of special interest. The more important of these are indicated in the table on page 338.

Future Possibilities

Extensive as is the application of phenol-formaldehyde resin, its use has been restricted by its relatively high cost. If its cost could be brought down to, or below that of less serviceable materials now employed

CHEMICAL PROPERTIES OF PHENOL-FORMALDEHYDE PRODUCTS

	Transparent	*Molded*	*Laminated*
Effect of:			
Organic solvents, such as acetone, alcohol, aniline, benzene, benzine chloroform, ether, naphtha and turpentine.	No effect	No effect	No effect
Oils	No effect	No effect	No effect
Acids, organic and dilute mineral	No effect	No effect	No effect
Alkalies	Cause noticeable softening and ultimate disintegration of resin		
Water absorbed in 24 hours	0.05 to 0.07	0.05 to 0.20	0.2 to 1.0
Age (with exposure to air and sunlight).	No depreciation in physical or electrical properties		
Heat	Does not soften appreciably up to 500° Fahrenheit, when the material begins to char; withstands a continuous temperature of 300° Fahrenheit.		

in the mechanical arts, its use would be vastly extended. The great obstacle in the way of a low cost is the high cost of its raw materials—phenol and formaldehyde—for which there have been found no satisfactory substitutes. These, though relatively cheap as drugs, are expensive as the ingredients of a substance to be used in place of common materials of construction. With cheap raw materials, a further lowering of cost would come through quantity production and labor-saving machinery.

Also much is still to be desired by way of the adoption of automatic presses having quicker heat transfer, since this would make for more rapid production and a saving in labor and equipment.

Progress along these lines of cheaper production is bound to come. In the meantime, there is need for work directed along lines of quality improvement. While phenol-formaldehyde resin is our strongest and most inert plastic, still improvement is desirable in the way of increased toughness. Also, while it is recognized as having good insulating properties, still there is no limit to the need for improved electric insula-

tion, whether to make possible the carrying of higher voltages in long distance transmission or to lessen the loss in those well-nigh infinitesimal currents that make radio the joy and wonder of these scientific times. All present insulation develops too low surface resistance when exposed to highly humid conditions, such as are found in the tropics and even in more temperate climes.

And so must research go on, to find new materials of value to man, and better and better methods of producing them so that their quality may be improved and their cost lessened.

In all this work great things may be expected of the American chemist, who already has to his credit many noteworthy achievements, not the least of which is commercial synthetic resin, a distinctively American product, both in its inception and in its development to the present high plane of industrial usefulness.

CHAPTER XX

CHEMISTRY IN THE RUBBER INDUSTRY

W. J. Kelly

Research Laboratory, The Goodyear Tire & Rubber Company

Historical

The earliest mention of rubber in European literature is to be found in some old Spanish and French accounts of explorations in Central and South America which were published about 1525 to 1530. It is also stated that Columbus saw balls made of rubber which the natives used in a kind of game that they played. These balls are described as being made of a black resinous material from the sap of certain trees. The natives of these countries also fashioned rough shoes from rubber and by treating cloth with the sap were able to make waterproof garments. Water jugs and other utensils were made on clay forms by dipping the forms in the sap and allowing them to dry. Even today such shoes and jugs are sometimes made by the natives of South and Central America.

For about three hundred years after the introduction of rubber to Europeans practically nothing was done to manufacture it in any way. Starting early in the last century, several people in Europe and America began experimenting in order to find some way in which this substance could be used commercially. The first attempts were crude but they started other men working on the problem until finally a treatment

which rendered the rubber suitable for many uses was invented by Charles Goodyear in 1839.

Before discussing Goodyear's invention it will be best to tell something of the origin and nature of this remarkable substance which holds a place second to none in importance in the everyday life of the human race.

Occurrence and Preparation of Crude Rubber

The rubber which appears on the market is prepared from the latex of many trees which grow exclusively in tropical countries. The latex is a milky liquid which exudes from any cut in the bark of the tree. By a regular method of cutting or tapping, as it is called, the latex can be conducted into small cups placed on the ground at the base of the tree. The latex which runs into these cups is then collected and taken to a central point where the rubber is separated from the water and other substances present in the latex. This method of collection is used exclusively where the best grades of rubber are obtained. It is also used for some of the inferior grades as well, but in many cases, especially where the latex is obtained from shrubs or vines, the whole plant is destroyed and the latex pressed out or the rubber dissolved in some liquid.

The rubber of the best quality all comes from one tree called *Hevèa brasiliensis*. This tree grows abundantly in the valley of the Amazon River in Brazil and from this place the seeds which were used to start the great plantations of the Far East were obtained.

The plantations are a development of practically the past twenty or twenty-five years. In 1900 there was scarcely any plantation rubber and none of it was on the market. Today the annual consumption of rubber

is about 350,000 tons of which more than 75 per cent comes from the plantations. These plantations are situated in Sumatra, Java, Borneo, Ceylon, and the Federated Malay States.

The methods used by the natives for separating the rubber from the latex differ according to the locality. The best rubber, which comes from the Amazon Valley and is known as Fine Para, is prepared by a smoking process. This rubber has the most uniform quality in some respects of all the rubbers on the market.

After the latex has been collected and taken to some central point the native builds a fire using a peculiar palm nut to give a dense black smoke. He then takes a paddle, dips it in the latex, and holds it in the hot smoke. This evaporates the water and leaves a thin film of rubber on the paddle. This operation is repeated over and over until there is a large lump of rubber weighing 60 to 80 pounds on the paddle. This lump of rubber is called a biscuit. It is then slit open and the paddle removed. In this form it comes on the market. The biscuit is not pure rubber as it contains some water and other substances which have to be removed before it can be used in the factory. The process by which this is done is called washing and after drying it is found that about 20 per cent of the original weight has been lost. The washing is done on a machine called the washer, which consists of two horizontal rolls about 24 inches long and 12 to 14 inches in diameter, having corrugated surfaces. The rubber is passed several times between these rolls under a spray of water. The rolls break up the rubber and form it into a sheet while the water removes any dirt, bark, and water-soluble material that may be present leaving a clean and pure rubber which, after

drying, is ready for further manipulation in the factory.

When the plantations started to produce rubber the chemist was called upon to devise cleaner and better methods to obtain the rubber and to obtain it in a form which would require no washing at the factory. In other words, he was asked to prepare a pure rubber at the plantation which would be all ready for use when it reached the manufacturer. Many people claimed that this could never be done, but the chemist found a way, and now more than 75 per cent of the world's rubber supply is prepared under the scientific control of the chemist.

The first thing the chemist did when he had a sample of latex was to examine it under the microscope. He found that it consisted of very small particles about one twenty-five thousandth of an inch in diameter suspended in the water. This is a case similar to many others known and which had been thoroughly studied. This particular class of systems is known as colloids and one of the properties is that the small particles are caused to clot together and separate from the liquid if certain acids or salts are added. A test was then made and it was found that acids and salts of an acid nature when added in small quantities to the latex would cause the particles to clot together and form a coherent mass which, being lighter than water, floated on the liquid. This liquid which remains is called the serum. Some of the serum remains in the rubber as the latter has a spongy structure and this is removed by passing the rubber through a washer several times. In this way the excess acid and serum are removed and the rubber is obtained in thin rough sheets called crepe. It is a pale yellow as contrasted with the dark brown to black biscuits of Fine Para.

It was then found by further experiments that the Fine Para rubber was still slightly superior to the crepe and it was thought that this might be due to the action of the smoke. Consequently some of the coagulated slabs were pressed between smooth rolls into thin smooth sheets and hung in a smoky atmosphere to dry. The resulting rubber was dark brown and was more nearly like the Fine Para. This type is called smoked sheets. Sometimes the rubber is simply rolled into sheets and dried without the use of smoke. It then appears on the market as unsmoked sheets.

Not satisfied with these methods of preparing a pure, clean rubber, the chemist continued his experiments and finally evolved two other methods, in which the water of the latex is evaporated by heat and all of the substances present in the latex are then left with the rubber. One of these processes consists in forming a very thin film of latex on the inside of a rotating drum and blowing warm air on it. The drum is rotated until a fairly thick layer is built up, when it is cut off in a sheet and the process repeated. The second method consists in spraying the latex into a hot chamber in the form of a very fine mist. The water is evaporated and the rubber falls to the bottom where it collects in a snow-like layer. It is then pressed and is ready for the market.

When these methods are compared with the smoking process of the South American native or with some of those used by the natives of Africa it can be readily seen what improvement the chemist has brought to this one phase of the rubber industry. As an example of African methods it may be mentioned that in many places the natives smear the latex on their bodies and the heat of the sun, combined with the body

heat and the acid in the perspiration, causes the rubber to separate from the water. Naturally, only inferior grades of rubber can be obtained in this way.

Early Methods of Manufacture

The pioneers in the manufacture of rubber were all beset with trials and tribulations unknown to their present-day successors. In the first place, all articles would become soft and sticky and lose their shape in hot weather, whereas in cold weather they turned hard and brittle and cracked easily. Imagine a raincoat which would stick to one's clothing on a hot day and crack open on cold days! The situation was much the same for all articles made.

The first efforts of the early manufacturers were confined principally to the coating of cloth with rubber for the purpose of making waterproof garments. To do this the rubber was first dissolved in some liquid like turpentine, petroleum, or coal-tar naphtha and the resulting solution or dough was spread on the fabric in very thin films. The solvent was evaporated and the rubber left on the cloth. The cloth, being coated on one side only, was made up into raincoats and other articles. Whichever side was turned out, the article would always stick to something in hot weather. Finally, a Scotchman by the name of Macintosh conceived the idea of folding the fabric so that a double layer of cloth with an intermediate film of rubber was obtained. This eliminated the sticking, but did not prevent the rubber from becoming hard and stiff on cold days.

It is easy to see that in order to make a commercial article from this material, some radical change in the processes would have to be invented or some chemical

change brought about in the rubber itself which would render it less susceptible to temperature changes. This was finally accomplished by Charles Goodyear in 1839.

Vulcanization

Before taking up the present methods of manufacture, it will be most fitting to describe briefly the process by which rubber was converted from a substance which could not withstand any great temperature change and which had comparatively little strength to one which would retain its elastic properties over very wide ranges of temperature, at least to one which retained these valuable properties within the temperature limits where it was usually used. This process is called vulcanization. It was invented by Charles Goodyear in 1839 after many years of study. Briefly, it consists of mixing a small percentage of sulfur with the rubber and heating the mixture to a temperature of about 140° Centigrade (286° Fahrenheit) until the desired properties have been obtained. During this heating the sulfur acts chemically on the rubber, and forms a new chemical substance or substances which have the properties that make the finished product so valuable. The vulcanized rubber is much stronger and more resistant to change of shape from external forces than the original unvulcanized material. The original rubber is soluble in many liquids such as naphtha, turpentine, carbon tetrachloride, chloroform, carbon bisulfide, etc., but after vulcanization becomes insoluble.

Goodyear originally mixed some white lead, lead oxide (litharge), or other lead compound with the rubber and sulfur, as he found that by this means a stronger and more durable product was obtained and

that the time of heating necessary to produce the desired result was considerably shortened. This process is the fundamental one of the present rubber industry, and it would be impossible to make any durable or satisfactory articles of rubber without it.

Simple as this process seems, the chemistry of it is still unknown. The little that is known about this reaction between sulfur and rubber will be treated later under "Theories of Vulcanization." Suffice it to say here that the explanation of the action of sulfur on rubber in all of the mixtures used in present-day practice is one of the most baffling problems that the chemist has ever tackled. Its solution will probably mean few changes, if any, in the methods of manufacture, but the chemist always wants to know exactly what is happening in the process he is handling and never rests until he has at least a good working hypothesis.

Present Methods of Manufacture

The first step in the manufacture of rubber articles, viz., washing, has already been described in connection with the preparation of the crude rubber.

The next operation is exactly the same as it was in Goodyear's time. It consists in grinding or masticating the rubber on a mill which has two horizontal rolls or cylinders running at slightly different speeds and in opposite directions. The surfaces of these rolls are about one-fourth to three-fourths inch apart at their nearest point, so that as the rubber passes between them it is rolled out into a sheet which adheres to one of the rollers, usually the slower one. The crude rubber is ground or milled until it forms a smooth,

soft sheet on the roll. The other materials are then added and the whole mass worked until an even distribution of the added ingredients is obtained. The mixed batch is then cut from the mill in large slabs and stored for further use.

Articles such as bumpers, erasers, some packing for certain valves, heels, soles, etc., are cut to approximately the correct size from the slabs or from sheets of the proper thickness and placed in molds. They are then subjected to high hydraulic pressure to insure filling all parts of the mold and heated by steam.

In many instances such as tires, hose, belting, etc., the rubber has to be put on cloth and the article is then built up from this prepared fabric. The rubber is usually put on the cloth in a machine called a calender, which consists of three horizontal rolls placed one over the other. The rubber is fed in between the top and middle rolls and the fabric between the lower and middle. In passing between the lower rolls the rubber is ground into the fabric and the threads are completely surrounded by a film of the rubber.

In some cases, especially in the manufacture of fabric for balloons, the rubber and sulfur are first mixed and then converted into a dough with gasoline. This dough is then spread on the fabric on a machine called a spreader. For some of the balloon fabrics as many as thirty coats are applied to insure the finished fabric against any mechanical imperfections or holes.

Chemistry plays an important role in these processes inasmuch as all but the spreading are carried out at elevated temperatures and hence the mixture or stock, as it is called, has to be so made that it will not vulcanize during these operations.

Compounding Ingredients

There are very few articles on the market today which are made from pure rubber vulcanized with sulfur. Literally hundreds of other materials, mineral and organic, are mixed with the rubber during the process of manufacture. Although some of these substances are added to cheapen the cost, most of them are used to obtain some specific result, either in the process or in the quality of the finished product. An automobile tire made from pure rubber vulcanized with sulfur would probably not run over a thousand miles. The tread would be too soft and would be ground away by the action of the roadway in a very short time.

The first compounding ingredient used was white lead, which not only increased the strength and toughness of the material but at the same time decreased the time necessary to effect a proper vulcanization. In the early days of the industry, rubber was a rather expensive material and in order to bring the price of the manufactured article within the buying ability of more people some materials called fillers were added to reduce the cost. These materials increased in number and a few years ago the composition of many mixtures used commercially was frightful.

When the chemist started to work on the action of these substances he found many questions which had to be answered. Some of these still remain unanswered, but many of the problems of compounding have been solved and the formulas now used in most of the large factories are considerably simpler.

Some pigments or powders added to the rubber were found to have a decided effect on the time required for proper vulcanization. Such substances as lead

oxide (litharge), white lead, zinc oxide, magnesium oxide, and lime (calcium hydroxide) were found to be in this class when used in small proportions.

Others, such as clays, barium sulfate, iron oxide, gypsum (calcium sulfate), lamp black, etc., had no effect whatever on the time of vulcanization. If, however, larger amounts were added it was found that each one had a different effect on the strength and toughness of the product when the amounts were such that equal volumes of pigment were added to the same volume of rubber. The first effect, viz., the shortening of the time of vulcanization, could be ascribed to the fact that each of the substances underwent a chemical change during vulcanization. The exact nature of this change and how it affects the rate of vulcanization is still unknown, although some progress has been made in solving this problem during the past few years. All these materials are basic in nature and hence have the power to neutralize acids. The resins contained in rubber have certain acids which are neutralized by the base, forming a salt which is soluble in the rubber. This salt then reacts in some way with the sulfur rendering it more active and thus increasing the rate at which the sulfur will combine with the rubber. A second effect of this same reaction is an increase in the strength of the union between the rubber and the mineral ingredient which results in a stronger product than would otherwise be obtained.

Further experiments on the chemically inactive ingredients showed that when compounded in equal volumes there was a very decided difference in the strength and toughness of the product. These substances being chemically inert, their action in stiffening the rubber could be physical only. Hence, the logical thing was to find out which of the physical character-

istics of these substances showed the greatest differences. A microscopic examination revealed the fact that the particle size of the dry powder was very much smaller in gas black, lamp black, and zinc oxide than it was in the case of barytes, calcium carbonate, clay, and other materials. Those pigments with the finest particles gave the strongest and toughest products. Some pigments which were known to be finer than others gave results which were inferior to the coarse-grained ones. Further microscopic examination showed that when such pigments were mixed with rubber there were large lumps consisting of many small particles distributed throughout the rubber. If these lumps were broken up and each individual particle was separated from the others the product assumed the place which would be assigned to it from a study of the size of its particles. Hence, there are two main properties which a good compounding ingredient should have: first, fineness of particle; and second, the ability to disperse completely in rubber.

Accelerators

There is another group of substances added to rubber which have a very decided effect on the time required for proper vulcanization. These substances are organic in nature and for the most part are nitrogen-containing bodies. They are used in small amounts, on the average about 1 to 1.5 per cent of the weight of the rubber, and some of them can make a mixture, which without accelerator would require two and one-half to three hours at 140° Centigrade for proper vulcanization, vulcanize in two and one-half to three minutes at the same temperature. Other substances are capable of effecting the vulcanization in practically

any desired time between the above limits so that the manufacturer has a powerful instrument in his hand with which to reduce factory costs.

Moreover, these same substances besides giving products which require less time for vulcanization also increase the quality of the product. The result is a better product obtained at a lower cost. This is one thing that the chemist always desires to achieve.

Some of these accelerators are simple organic bases such as aniline, toluidine, piperidine, etc., while others are very complicated like the products obtained from the action of aldehydes on the above bases. Diphenylguanidine is one of the most popular as it gives a product of good quality in a reasonable time.

Although the reactions which take place between these accelerators, sulfur, and other substances in the rubber have not been fully cleared up, a great deal of work has been done on them. The principal result of this work is that in many instances it has led to the discovery of new accelerators among the complex organic substances, and many of these are being used today whereas a few years ago they were very rare and existed only as laboratory specimens. A fairly large industry, that of manufacturing these organic accelerators, has been built up as a result of the rubber chemist's investigations. New accelerators are being discovered every day, many of them useless, but the work of investigation goes on and sufficient new facts are discovered to assist in the final explanation of acceleration and vulcanization towards which most rubber chemists are working.

Theories of Vulcanization

Since the process of vulcanization was invented by Goodyear many chemists have studied it from the

theoretical standpoint. The first man to propose a theory for the action of sulfur on rubber which was based on a real scientific investigation of the reaction and its product was C. O. Weber. In carrying out this work Weber vulcanized samples of rubber with varying amounts of sulfur for different lengths of time and at different temperatures, and then determined the amount of sulfur which had combined with the rubber chemically and hence could not be removed from it by extraction or dissolving it in acetone.

If more than fifty parts of sulfur were mixed with one hundred of rubber and vulcanized for long times Weber found that the product contained a maximum of 32 per cent of sulfur or forty-seven parts per one hundred of original rubber. Under no circumstances was Weber able to make a product with more than this amount of sulfur. The product thus obtained was hard rubber, such as is used today in fountain pens, battery jars, bowling balls, and hundreds of other articles of everyday use. Weber naturally concluded that this must be the final product of the reaction between rubber and sulfur and that other products obtained with less sulfur would then be intermediates of some kind. These results were confirmed later by Spence and others so that we may take it as proved that the highest product of vulcanization has a definite composition.

With the soft rubber goods the matter is entirely different and up to the present no one has been able to say definitely what takes place when sulfur acts on rubber.

Weber attempted to explain this action on the basis of some observations. He noticed a decided change in the physical properties of rubber as the vulcanization progressed. These changes first became really notice-

able when about 2.3 per cent of sulfur had combined with the rubber. On this basis Weber calculated that the formula of the substance thus obtained would be $(C_{10}H_{16})_{10}S$, which contains 2.29 per cent of sulfur. Between this product and the final one with 32 per cent of sulfur or $(C_{10}H_{16}S_2)_{10}$, Weber suggested that there was a series of compounds each containing one more sulfur atom than the preceding one.

The two main objections to this theory were: First, in most cases where chemical changes occur in stages, the physical changes do likewise and in rubber the physical changes, such as increase in strength, were all continuous smooth curves; and second, no one of the compounds suggested by Weber has ever been separated from the rest of the rubber. Since Weber's time rubber chemists have succeeded in making perfectly vulcanized products by the use of accelerators containing less than 1 per cent of combined sulfur, and hence the first part of Weber's theory can no longer be considered valid. Furthermore, no one has ever been able to discover any definite relation between maximum physical properties and the amount of combined sulfur.

These and other facts led Wolfgang Ostwald in 1912 to propose a new theory of vulcanization based on the assumption that sulfur did not react chemically with the rubber but that it was adsorbed on the surface of the rubber particles. This theory has so many defects that it is not worth while to discuss it.

At present many rubber chemists are at work trying to formulate a theory which will cover all the facts known about vulcanization. This will have to include the physical nature of the rubber itself, the reaction with sulfur, the change of physical properties, the action of accelerators, and many other factors. The

problem will finally be solved by attacking it at several different points, physically and chemically, and most of all from the colloidal viewpoint. The solution of this problem will possibly mean that new tricks in factory practice will be discovered which will enable the manufacturer to cheapen his process without changing the quality of his product.

Reclaiming Rubber

Another chemical process which is of great importance to the rubber industry is that of reclaiming old rubber so that it can be used again. The scrap tires, belts, shoes, etc., all have a great deal of cotton in them which must be removed. This is usually done on scrap which has been ground fairly fine. The ground scrap is put in large kettles and heated with a dilute solution of sulfuric acid or sodium hydroxide. Both of these agents destroy the cotton so that it can be washed out with water.

The alkali process is carried out in large heaters in which the material can be heated under pressure so as to raise the temperature considerably above the boiling point of the solution. The action of the alkali destroys the cotton and the heat softens the rubber so that it can be used again. At the same time any free sulfur, which is always present in vulcanized rubber, is removed by the action of the caustic. Sometimes oils are added to assist in the softening of very hard stocks, such as solid tires, tire treads, etc. This renders them more plastic and hence more adaptable to further use in the factory.

The exact action of the alkali on the rubber in this process is not known and whether it is the heat alone or the action of heat and caustic which softens the

rubber is still to be determined. There are many problems to be worked out in these processes which will vitally affect and probably cheapen the methods and at the same time yield a better product.

Recapitulation

Taken all in all there is a vast amount of work for the rubber chemist to do before any of the processes carried out in the factory are fully understood from the physical and chemical standpoint. These unsolved problems include the structure of the rubber itself, the structure of vulcanized rubber, the course of the reaction between sulfur and rubber, the reactions of accelerators, the causes of the effects of accelerators, the changes which take place in reclaiming, the action of the compounding ingredients, and many others. The solution of any of these means that the industry will advance from the practical side and give the public better products. It is therefore easy to see that the chemist and the physicist have enormous problems before them and they are working with all their power to solve all of them. The answers will be forthcoming some day and the sooner the better for producer and consumer alike.

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CHAPTER XXI

CHEMISTRY IN THE TEXTILE INDUSTRY

L. A. Olney

Professor of Chemistry and Dyeing, Lowell Textile School, and President of the Stirling Mills and of the American Association of Textile Chemists and Colorists

It would be a difficult matter to find many people who have not been attracted by the seasonable displays of highly colored and lustrous textile materials exhibited from time to time in the spacious windows of our modern department stores, and who have not, even though in a hurry, stopped to admire the latest developments which always appear to rival those of previous years in splendor and attractiveness. How many, however, appreciate the fact that these marvelous displays are due almost entirely to the development of the science of chemistry and its diversified applications. Eliminate chemistry and the knowledge and skill of our color and textile chemists, and these same windows would either be empty or filled with unbleached cotton cloth and lusterless and dull-colored fabrics of the homespun variety.

Early History

The history of the development of the textile industry is filled with many interesting incidents, some of which may almost be styled as romances. Among such may be mentioned the discovery of the first coal-tar

dye by Perkin, the development of synthetic indigo, the discovery of the process of mercerization and its later adaptation for the production of luster, and the invention of artificial silk.

The early dyers depended entirely upon vegetable matters, such as the extracts of barks, roots, and nuts, a number of mineral substances, such as iron oxide, chrome yellow, and Prussian blue, and at least one substance of animal origin, namely, the cochineal bug. Yellows and browns predominated, but with madder root the celebrated Turkey red was produced, the indigo plant produced the blues very largely, and greens were frequently made by combining indigo with one of the yellows. With their limited possibilities they had remarkable success in producing attractive effects, but the great brilliancy and almost unlimited variety of shades characteristic of today were lacking. It is interesting to note that these old-time dyers, although for the most part uneducated as far as the sciences were concerned, unconsciously relied upon the application of chemical principles in the development of all of their dyed textiles, and while all the great advances in textile chemistry and in the manufacture and application of dyes have been made within the past eighty years, the pioneer efforts of thousands of early dyers, a few of whom left records of their work and experiments, were important contributory factors towards these later developments.

Discovery of First Coal-Tar Dye

In the year 1856, Sir William Henry Perkin, then a student in chemistry at the Royal College of London, was at home for his spring vacation. Vegetable quinine had just been introduced as a valuable specific for

malaria, and he conceived an idea that it might be produced chemically. As a result, he spent most of his vacation experimenting in a home laboratory with this object in mind. At one stage of his experiments a decidedly purplish color developed, which interfered somewhat with his progress. Being unable to avoid this characteristic discoloration he finally turned his attention to its scientific study, and from this accidental and rather unexpected incident there resulted the discovery of mauve, the first of the so-called coal-tar dyes. The interesting results of Perkin's work and its apparent commercial possibilities immediately awakened great interest among chemists, and it was not long before magenta was discovered, and a little later methyl violet, and the manufacture of coal-tar dyes became an industry. Thus a youth of eighteen had the honor of originating one of the most important branches of chemical industry, and upon the jubilee celebration of this event Sir William Henry Perkin, who was still alive, was honored both abroad and in this country by numerous celebrations and functions suitable to the occasion.

In order to make the commercial development of color manufacture possible, another industry was absolutely essential, namely, that of the manufacture of coal gas, for this gave rise to the by-product known as coal tar. This coal tar was at first the despair of the gas manufacturer, and its disposal at one time became such a nuisance that it almost looked as though gas manufacture would have to be abandoned. Fortunately, however, it was discovered that a great variety of products could be obtained from coal tar through subsequent distillations, and several of these, notably benzene, toluene, xylene, naphthalene, and anthracene are the fundamental crudes of the color

industry. From these crudes there are made, oftentimes through rather long series of reactions, the so-called intermediates, which now number three hundred or more. By still further and frequently rather complicated chemical reactions, two or more of these intermediates are combined to produce the ultimate dye. The crudes used are almost entirely colorless, as are also a large proportion of the intermediates, and their chemical composition is changed or modified many times previous to the final development of the dye. It will thus be seen that the relationship which exists between a coal-tar dye and coal tar itself is merely one of source, for there is nothing about coal tar itself which in appearance or chemical composition resembles the finished dyes.

Since the memorable discovery of Perkin, more than fifteen hundred different dyes have been made and used, although many have now become obsolete. Mauve, for instance, has long since ceased to be of commercial importance, having been replaced by other coal-tar dyes which, for one reason or another, were found to be more desirable.

The whole history of the coal-tar dye industry reads almost like a fairy tale. Fortunes and reputations have been made, organic chemistry has developed to a high standard largely through its influence, and the agricultural interests of one of the biggest countries on the globe have been largely reorganized because of it. Perhaps no one dye illustrates all this better than indigo.

Development of Synthetic Indigo

Indigo has been a favorite blue dye for thousands of years, this dye having been used in connection with

coverings of some of the oldest mummies found in Egypt. The indigo plant was cultivated in India for many years. With the aid of British capital, and a constantly increasing use throughout the world, its cultivation had grown to a remarkable extent and had become one of the most extensive and most profitable agricultural pursuits of the Empire. Furthermore, its distribution all over the world had become an important factor in commerce. In 1868 Graebe and Lieberman prepared alizarin (the coloring principle of madder root used in the production of Turkey red), and this rapidly replaced the natural product which had been used for coloring purposes almost as long as indigo. The commercial success of this undertaking led color chemists to hope for a similar development in regard to the synthetic production of indigo from coal-tar derivatives. Many of the best minds puzzled over this problem for years, but finally, in 1880, Adolf von Bayer, a German color chemist, established its chemical formula and worked out a method for producing it in the laboratory. Its commercial production at a price low enough to compete with natural indigo was another matter, however, and several processes were tried and abandoned one after another, before it was finally put upon the market, and sold, at as low a price as the natural indigo, without a loss. It has been conservatively estimated that before the first pound of synthetic indigo could be sold at a profit, the Badische Company had spent five million dollars, but when its production was once established upon a paying basis the cost was continually reduced, and by 1914 the synthetic indigo had almost driven the natural product from the market, not only on account of lower cost, but because it was a purer and more reliable product. While the downfall of the indigo industry

of India assumed almost the proportions of a financial disaster, it was perhaps a blessing to India from an economic point of view, for no less than a million acres of land were made available for the production of foodstuffs and the famine probabilities have been greatly reduced.

With the exception of logwood, which is still extensively used for dyeing wool black, and fustic, a yellow dye frequently used in connection with logwood, most of the so-called natural dyes have for the most part gradually passed out of use and been replaced by the manufactured organic dyes produced from coal-tar derivatives. If we leave logwood and fustic out of consideration, probably 98 per cent of all textile dyeing is done with coal-tar dyes.

Variation in Action of Dyes

This transition has been gradual and in most instances by no means so spectacular as the downfall of vegetable indigo and the introduction of the chemically manufactured product. In this connection it is well to note that in the cases of alizarin and indigo the synthetically produced dyes are identical in chemical composition with those they replaced, but in most every other instance the natural dyes have simply been abandoned and coal-tar dyes of an entirely different nature have taken their places.

Should we have several hundred coal-tar dyes placed before us in the laboratory, and then attempt to dye various textile materials with them, we should soon discover that many of them act quite differently, and furthermore, that in many instances the same dye has an entirely different reaction toward different fibers. Some of these dyes would dissolve in water, and from

such a water solution readily dye both cotton and wool; others would dye wool, but not cotton. Furthermore, some would prove to be insoluble in water and have no affinity for either cotton or wool. The former are in a general way classified as *direct dyes,* and the latter, which require the fixation of some secondary substance upon the fiber to attract and hold the dye in permanent combination, are known as *mordant dyes.* We should find other dyes, known as *sulfur dyes,* which although insoluble in water will dissolve in an alkaline solution of sodium sulfide, and others known as *vat dyes* that could not be dissolved until they had been subjected to a rather energetic alkaline reduction. When once in solution, however, they take on the general properties of direct colors, although with all of the vat dyes, and to a certain extent with some of the sulfur dyes, a subsequent oxidation is necessary to develop and fix the dye upon the fiber.

The pronounced variation in the action of dyes toward different textile fibers depends almost entirely upon the difference in the chemical composition of the latter. Thus the vegetable fibers, composed mostly of cellulose or related compounds, contain no nitrogen and act entirely different from wool and silk, which are highly nitrogenous in character. Artificial silk is also dyed very extensively, but this for the most part acts like cotton, being fundamentally cellulose, although one type of artificial silk, the cellulose acetate variety, differs somewhat from the others.

The variation in the affinity between different fibers and different dyes is so great that it is a simple matter to dye the animal fiber in a fabric almost any desired color, and leave any vegetable fiber which it may contain perfectly white; or, by the proper selection of dyes, the animal fiber, wool, or silk, may be dyed one

color and the vegetable fiber, usually cotton, an entirely different color in one and the same dye bath. By introducing certain types of artificial silk it is even possible to produce three different colors in the same fabric with only one dye bath.

Prejudice against American Dyes

Ever since coal-tar dyes were introduced, misunderstandings of one kind or another have led the general public to adopt a rather critical attitude toward them. Some of the very first coal-tar dyes were extremely fugitive to light, not being able to withstand more than a day of bright sunlight without fading, others were no faster to washing, and some were neither fast to light nor washing. A popular prejudice was thus aroused against them at the start, and with the help of the sellers and users of natural dyes, particularly the dealers in oriental rugs, this was continued for many years. In more recent years an antagonistic attitude toward the coal-tar dyes of American manufacture has been quite the popular thing, particularly on the part of certain importers of foreign textile materials and deluded store clerks. Such criticisms are unjust and, for the most part, without foundation. The facts of the case are briefly these.

Many of the earlier dyes were unsatisfactory for some purposes, but as time went on, color chemists turned their attention very largely towards the development of faster dyes, and one after another the earlier dyes were replaced by those which were more satisfactory. Among the natural dyes none were considered more satisfactory and faster than madder for the production of reds, and indigo for blues, but as has already been stated these were eventually made syn-

thetically and actually became members of the criticized group of coal-tar dyes. Through the developments of the past twenty-five years the coal-tar color industry has been brought to a point where it may be said without danger of contradiction that it is now possible to reproduce with coal-tar dyes any shade that was ever dyed with natural dyes, and have it equally fast and, in most instances, faster than those produced by the latter. Furthermore, innumerable shades and tints were made possible with coal-tar dyes which exceeded even the fondest imagination of the user of natural dyes.

In this connection it must be remembered that a pronounced variation exists among the properties and relative fastness of the individual members of the long list of coal-tar dyes. Some are extremely fast in one respect and perfectly satisfactory for some particular purpose, but fugitive in another respect and wholly unsuitable for certain other purposes. Satisfactory results are, therefore, very largely a matter of proper choice of dyes. When the war came so suddenly in 1914 the United States probably manufactured not more than 10 per cent of the dyes she consumed, and the supply of imported dyes soon became much depleted. As a result, American textile manufacturers were frequently forced to use dyes which were unsuited for their particular purpose, and thus much dissatisfaction arose during the war period. These unsatisfactory results, however, were fully as likely to have been brought about through the use of left-over German dyes as of those of domestic make, but the American manufacturer naturally had to take the whole blame. Today, the United States is manufacturing more than 90 per cent of the dyes she consumes, and these are in every way as good as those previously

imported from abroad. The remaining 10 per cent can be imported if necessary. Thus there is absolutely no reason why American-made colored goods should not be exactly as fast as they were before the war, or as foreign-made colored goods are today. Unsatisfactory results, therefore, cannot be laid at the door of the American dye manufacturer, and oftentimes not even upon the textile manufacturer, for he may be forced to use cheaper dyeing processes than he would prefer, on account of the unwillingness or inability of the buying public to pay the higher cost of a faster grade of dyed material.

Dyeing and Printing Textiles

In the application of dyes to textile materials two quite different methods of procedure are in vogue. The most common of these is called dyeing, and includes any process where the entire material that is being colored is immersed beneath the surface of the dye bath for a definite period of time. The material may be in the form of cloth, in which case the process is known as piece dyeing; in the form of yarn, in which case it is known as warp or skein dyeing, depending on the form in which it is handled; and in the loose or unspun state, when the process is called stock dyeing. In all these cases the material is dyed a solid or uniform color all over and if a two or more color effect is produced it wholly results through the process of weaving. In the other method the color or colors are confined to certain portions of the fabric by a process of printing. In the earlier days of the industry, printing was done by means of blocks which worked on the same general principle as rubber stamps, though of course much larger, but modern printing is done by means of en-

graved copper rolls, as many as sixteen different colors being printed at one time. By the process of textile printing it is possible to produce very elaborate colored designs, the cost of which, if produced by a weaving process, would be prohibitive or which, on account of complicated design, would be impracticable to produce in any other way.

Bleaching Textiles

The application of color is not the only element contributing toward the attractiveness and salability of textile materials. In some instances the total elimination of color by a bleaching process is as effective as the addition of color and the introduction of luster, either by the use of some naturally lustrous fiber or by artificial means, is extremely effective. In fact, the development of both of these factors has involved in many ways as much chemistry as the process of textile coloring.

Bleaching is for the most part an oxidation process but in the case of wool a reduction process is more frequently used. Chlorine, in the form of hypochlorites, and also certain peroxides, usually of hydrogen or sodium, are most commonly used as oxidizing agents, and sulfurous acid most frequently as a reducing agent.

Mercerization

For several thousands of years silk fiber has been noted for its remarkable luster when properly treated and finished. The high cost of this fiber, however, has been responsible for many attempts to imitate or produce a similar luster in a cheaper manner. The most successful commercial methods for creating a

high luster are through the mercerization of cotton, the Schreiner finishing process, and the use of artificial silk.

The whole history of mercerization and its various applications presents a wonderfully interesting story which, briefly told, is as follows. John Mercer, an English calico printer, in 1844, while attempting to filter a solution of caustic soda through a piece of cotton cloth, noticed that while the solution ran through quite rapidly at first, it always went slower and slower and in a comparatively short time would almost entirely cease to go through. Being of a scientific turn of mind, he made an investigation of all the facts of the case, hoping to determine the cause. He found that cotton fibers, which under normal conditions were decidedly flattened in structure, swelled up and became round and almost cylindrical in appearance. He also found that as a result of this action cotton cloth shrunk about 20 per cent, became much stronger and more durable, and also had an increased affinity for many dyes. Mercer took out patents for treating cotton material with caustic soda solution which were considered of great value at one time. It is said that in 1852 he was offered two hundred thousand dollars for them, but refused to sell. The process of treating cotton cloth by Mercer's original process, however, did not prove to be very profitable and in a few years its use was almost entirely abandoned. Strange to say, Mercer entirely overlooked the most valuable fact of all, namely, maintaining the cotton material under tension while it was being subjected to the action of the caustic soda solution. It was not until nearly fifty years later that it was discovered that if the cotton material was rigidly held so it could not shrink during the action of the caustic soda, or thoroughly stretched before the

caustic solution was washed out, that a decidedly silky luster resulted. This treatment constitutes the modern process of mercerization, which is today one of the most important and profitable branches of the finishing of both cotton yarn and cloth.

While a decided chemical modification of the cellulose of the cotton takes place during mercerization, the development of luster is largely of an optical nature. It has been found that a transparent curved surface always reflects a pronounced line of light, as will be noticed by the examination of a glass rod. Upon mercerization the cotton fibers assume to a certain extent a transparent rod-like structure and if the yarn has been suitably spun the tension will keep these fibers more or less straightened and in a parallel position, both of which conditions seem quite essential for the development of the best luster.

Schreiner conceived the idea that if the surface of cotton cloth could be so embossed as to present innumerable curved or cylindrical surfaces all parallel to each other, a high luster would be developed. This he found to be a fact and today the process named after him consists in passing cloth under enormous pressure under a heavy steel roller which has been engraved with several hundred parallel lines per inch. This process is frequently combined with mercerization when an exceptionally high luster is obtained.

Artificial Silk

Among all the triumphs in chemistry in connection with the textile industry probably none is more spectacular than that of the manufacture of the various types of so-called artificial silks. In the strict sense of the word, however, these are not artificial silks, for

although the spinning process of the silkworm is imitated to a considerable extent in their production, the chemical composition of the substances of which they are formed is not comparable in any way with that of true silk. This fact has quite recently led to the introduction of the term "Rayon," as a commercial designation for these fibers as a group.

In spinning its cocoon the silkworm ejects through an extremely fine spinneret a semiliquid substance which possesses the property of hardening almost immediately into silk fiber. Count Chardonnet was the first to take advantage of a chemical reproduction of this process. He conceived the idea of taking a solution of collodion, which is nitrocellulose dissolved in an ether-alcohol solution, and forcing it through a very fine capillary opening. As soon as this substance was emitted from the spinneret the alcohol and ether rapidly evaporated, leaving behind an extremely fine fiber which was found to possess a luster even higher than that of true silk. In this form, however, the silk was extremely inflammable, but this was overcome by various chemical treatments known as denitration, so that the final product was little, if any, more inflammable than ordinary cotton. The success of the Chardonnet process led others to experiment along different lines, and while all of these further experiments involved the same physical principle of forcing a semiliquid substance through a fine capillary opening, the nature of the spinning substances used varied considerably. Hence the different varieties of artificial silks which are now on the market.

Of these there are four important varieties: first, the nitrocellulose silk which has already been mentioned; the viscose silk; the cuprammonium product; and, finally, that manufactured through the use of

cellulose acetate. The viscose or cellulose thiocarbonate silk is produced from a solution prepared by first treating cellulose, either in the form of wood pulp or cotton, with caustic soda and then with carbon bisulfide, the result being a rather thick, viscous liquid which has the property of solidifying when forced in the form of a fine filament into various chemical solutions. The cuprammonium silk is made from cellulose dissolved in an ammoniacal solution of copper hydrate which is solidified by forcing it through a solution of acetic acid. The cellulose acetate silk exists in several commercial modifications, among which might be mentioned Lustron and Celanese, and is manufactured through the use of cellulose acetate dissolved in one of several solvents. The first three types of silk mentioned possess more or less common properties and in dyeing act quite similarly to ordinary cotton, but the last, namely, the cellulose acetate silk, differs considerably, and in some of its forms it completely resists the absorption of certain dyes which are readily taken up by the others. In this way, a combination of two different artificial silks in the same fabric may be used for the production of two-color effects. On the whole these artificial silks are not nearly so durable as true silk and when wet their tensile strength is greatly reduced, but if properly made they possess a higher luster and are well suited for many purposes for which true silk could not be used on account of its high cost. As a rule textile fabrics are not made entirely of artificial silk but usually in combination with some other fiber, particularly cotton. A reasonable amount of artificial silk added to a cotton fabric oftentimes greatly increases the attractiveness of its appearance without seriously adding to its cost. Attempts to manufacture similar fibers using nitrogenous compounds

more comparable to silk substance itself have only been successful in a very limited experimental way, and have never proved to be a commercial success.

Future Opportunities

Taken as a whole there is probably no branch of industry which involves the use of a greater variety of chemicals and chemical reactions than that of bleaching, dyeing, printing, and finishing textile materials, and one who trains himself for the profession of a textile chemist and colorist must through necessity have attained such a thorough knowledge of the fundamentals of the science of chemistry and its applications, that he may readily adapt himself to most any other branch of industrial chemistry if later it is found desirable or necessary.

We must remember that all of these developments in textile chemistry and coloring have not been due to the brilliancy or knowledge of any one man or even a small group of men, but to the individual contributions of a multitude of chemists and colorists over a period of several hundred years. There are still many opportunities for further discoveries and few fields offer greater attractions for chemistry students of today than the applications of this science to the textile and color industries.

Date Due

O 22 37
My 27 '40
FEB 10 '44
FEB 28 '44
MAY 9 1945
MAY 23 '50
OCT 23 '51

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